A FIRST
CHEMISTRY

W. WILLINGS

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BY

W. WILLINGS, B.Sc.

Senior Science Master, Municipal
Technical School, Brighton
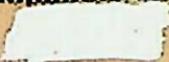
PREFACE

The object of this book is to provide a course in
Chemistry dealing mainly with the elementary facts of
the subject and only to a small extent with the theory
by which it is sought to explain these facts. For the
facts are abiding, while our explanations of them vary
from age to age. The attitude of young students
towards nature is that of the interested observer of
phenomena, able to draw simple conclusions from such
phenomena, but not, as a rule, able to understand or
appreciate the theory and measurements which have
raised Chemistry to the position of an exact science.

Hence many teachers believe that a first course in
Chemistry should not deal with the atomic theory and
its consequential equations, but should concern itself
mainly with an investigation of the composition of
bodies, their analysis and synthesis. The course covers
the syllabus of the Matriculation Examination of Madras
University and that of the Secondary Schools' Leaving
Certificate (India). Chapters XXI and XXX have been
included to meet the requirements of these examinations,
but they might with advantage be omitted by young
students.

In the text no attempt has been made to separate the
laboratory experiments from the discussion of the results

and the collection of the information gained. The aim throughout has been to develop the elementary theory of the subject by the consideration of the results of suitable experiments. The experiments yielding qualitative results present comparatively little difficulty. It is advised that the results obtained by the students should be made the basis of a class discussion with a view to drawing legitimate conclusions and suggesting experiments designed either to test the correctness of such deductions or to investigate the matter further. Where the results of the experiments are of a quantitative nature, although the methods and skill of the students may not permit of the high degree of accuracy needed to establish a generalization, they should be sufficiently accurate to confirm the generalizations based upon the more accurate determinations of skilled experimentalists. For this reason, the methods employed and the results obtained by eminent chemists have been described when it was thought to be desirable.

In dealing with quantitative results obtained by the students, it is advisable to collect the results of the whole class, reject any which are not in substantial agreement with the remainder, and take the mean value of the remainder; in this way a very fair degree of accuracy may be obtained. The results given in this book are the actual results obtained in this way with the ordinary apparatus found in a well-equipped Secondary School. The importance to be attached to the agreement amongst the results obtained by the different members of the class will naturally be insisted upon when the results are discussed. When there is any serious discrepancy between the mean class result and the accepted result of an evaluation, the students should

be encouraged to criticize the method of conducting the experiment, with a view to suggesting means of eliminating the errors inherent in the method adopted.

In the later part of the book the experiments have not usually been differentiated from the remainder of the text, but it is intended that wherever possible the statements made should be experimentally verified.

The view has not been lost sight of that the value of science teaching in schools consists mainly in the insight into scientific method which is given, and in the development of the scientific attitude of mind which it is hoped will remain long after the mere information so obtained is forgotten.

The order followed may not always appear to be strictly logical, although the aim has been to present the facts in logical sequence. The object has been to regard the development of the subject from the point of view of the pupil. For convenience of arrangement of the subject-matter, the common metals have been considered together at the close of the book. It is, however, advisable to commence the study of these metals and their compounds soon after Chapter XIV, and to study them simultaneously with the non-metals described in Chapters XV–XXI. The different methods of preparing corresponding salts of the metals is often very puzzling to the young student. The general methods of preparation given in Chapter XXIX will, it is hoped, help those who experience this difficulty.

A large number of the questions which appear at the end of the chapters are taken from the examination papers set at Oxford Local Examinations (O. L.) and the Cambridge Local Examinations (C. L.) The author takes this opportunity of thanking the Delegates of the Uni-

versity of Oxford and the Syndics of the University of
Cambridge for their kind permission to print the ques-
tions referred to.   At the same time he desires to express
his indebtedness to Dr. Charles Draper for many valu-
able suggestions during the writing of the book and
for his kindness in reading the proofs.

<div align="right">W. W.</div>

MUNICIPAL SECONDARY SCHOOL,
         BRIGHTON.

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A FIRST CHEMISTRY

CHAPTER I

APPARATUS. THE BALANCE, ETC.

In the study of Chemistry, the science which deals with the composition of bodies, we shall have occasion to use many unfamiliar articles. These articles—pieces of apparatus as they are called—will be described and illustrated as we have need to make use of them. We will commence with a description of what is perhaps the most important piece of apparatus the chemist uses—the balance.

Experiment 1.—To examine a balance.

When the balance is not in use the handle H is turned to the left, as in the diagram (fig. 1). This is the "position of rest" of the balance. When the balance is in the position of rest the beam B is supported by the screws S, S.

When the handle is turned completely over to the right a rod inside the tube P is raised, and this lifts the beam B off the supporting screws. The beam is then supported at its centre on a triangular piece of hard material—generally made of agate or steel—called a knife-edge because of its shape. This knife-edge rests either on a flat piece of agate or in a steel notch at the top of the rod inside P. Attached to the beam is a pointer A, which moves in front of the scale C.

The scale-pans E, E are suspended from stirrups F, F, which are fitted with steel or agate notches into which fit knife-edges attached to the beam. When the balance is in the position of rest the scale-pans rest on the wooden base of the

instrument, and the screws s, s bear the weight of the beam. This prevents the wearing away of the knife-edges when the balance is not in use.

The beam and scale-pans are balanced on knife-edges in order to make the balance sensitive; that is, to cause the pointer to move across the scale for a very small difference
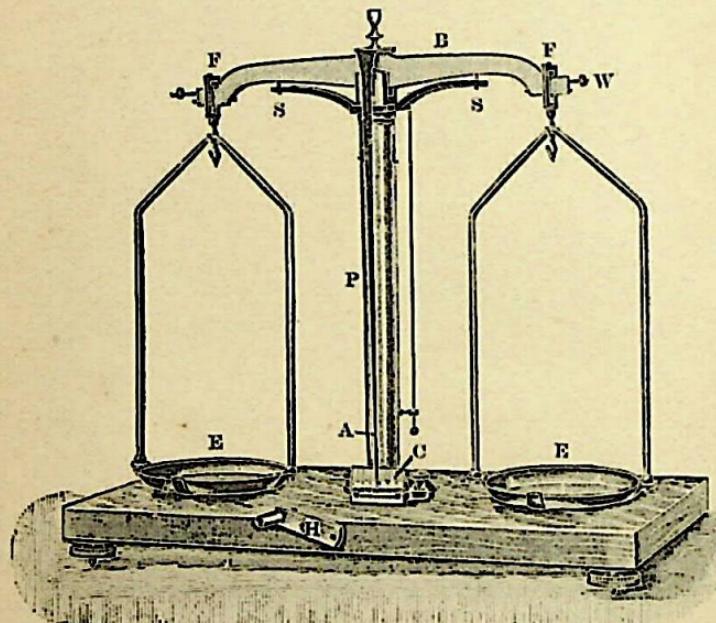
Fig. 1.—Chemical Balance

in weight between the loads on the two scale-pans. Anything which serves to wear away or damage the knife-edges makes the balance less sensitive. Therefore, when the balance is used—

(a) *the handle must be turned gently,* so as to avoid jarring;

(b) *nothing must be put on or taken off the pans unless the balance is in the position of rest.*

Experiment 2.—To adjust the balance.

See that there is nothing on either pan of the balance.

Turn the handle completely over to the right, and observe the pointer.

After the pointer has swung from side to side a few times, notice how far it swings on the left and how far it swings on the right of the central point of the scale. These distances should be equal.

Turn the handle to the left and so bring the balance to the position of rest.
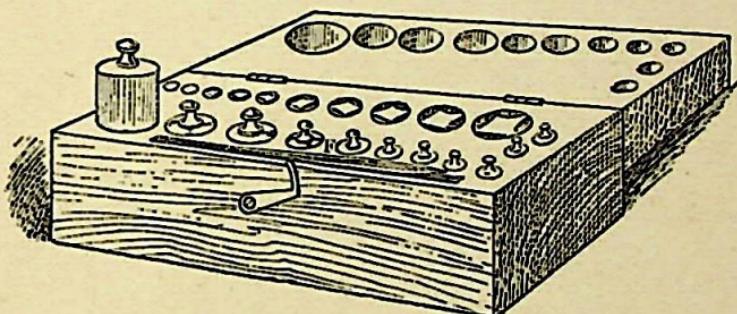
Fig. 2.—Box of Weights

If the successive swings of the pointer, left and right, were not equal, the small nut w (fig. 1) at the end of the beam must be screwed either outward or inward—inward if the pointer swung farther to the left than to the right. When the nut has been altered so that the pointer swings equally on each side of the central point of the scale, the balance is adjusted.

Weights.[1]—Examine a set of weights (fig. 2) and learn
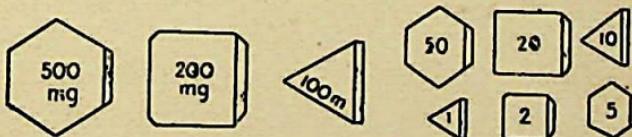
Fig. 2A.—Milligram Weights

the values of the weights and their positions in the box. Learn also to recognize the values of the small weights

[1] The quantity of matter in a body is called the mass of the body. The force with which the earth attracts a body is called the weight of the body. The term "weight" is commonly but erroneously used when "mass" is meant. In accordance with the general usage the term "weight" is used instead of "mass" in this book.

(milligrams) by their shapes. Notice that there are two 20-gramme (grm.) weights, and two 2-grm. weights. This is for convenience.

The small weights are marked in milligrams (mg.). (Fig. 2A.) The box contains—

one 500-mg. weight = ·500 grm.,
two 200-mg. weights = ·200 grm. each,
one 100-mg. weight = ·100 grm.,
one 50-mg. weight = ·050 grm.,
two 20-mg. weights = ·020 grm. each, and
one 10-mg. weight = ·010 grm.

Notice that—

the 500- and the 50-mg. weights are hexagonal in shape,
the 200- and the 20-mg. weights are square, and
the 100- and the 10-mg. weights are triangular.

The box also contains a pair of forceps F (fig. 2), which are to be used to take hold of weights when transferring them from the box to the scale-pan or from the scale-pan to the box. *On no account must the weights be lifted or even touched with the fingers.*

We will next proceed to use the balance to find the weight of some small object. Before doing so, however, note the following precautions, which must always be observed when using the balance:—

(i) *Do not weigh anything unless it is as cold as the air.*

(ii) *Do not place chemicals which are to be weighed directly on the pan of the balance;* weigh them on a watch-glass or in a small glass bottle.

(iii) and (iv) See (*a*) and (*b*), p. 2.

Experiment 3.—To find the weight of a watch-glass.

See that the watch-glass is clean and *dry*, and that the balance is adjusted (Experiment 2).

Place the box of weights to the right of the balance, and put the watch-glass on the left-hand pan.

Select a weight which you judge will be heavier than the watch-glass—say 20 grm.—and by means of the forceps, place it on the right-hand pan. Turn the handle of the balance to the right. If the pointer moves to the left of the scale it indicates that 20 grm. is heavier than the watch-glass.

Turn the handle to the left and replace the 20-grm. weight in the box. Place *the next smaller weight* in the box—10 grm. —on the scale-pan and see whether it is heavier than the watch-glass. If it is, try *the next smaller weight* in the box— 5 grm.

At length you will find a weight which is not as heavy as the watch-glass; the pointer will then move to the right. Place in the pan alongside this weight *the next smaller weight* in the box. If the two weights together are heavier than the watch-glass, replace the second weight by *the next smaller weight* in the box. If they are not as heavy as the watch-glass, place the next weight in the box with them. Continue to add weights as described, until, on turning the handle to the right, the pointer swings equally on both sides of the centre of the scale. Then turn the handle to the left.

Now look at the box of weights, and write down the values of the weights which are missing from the box.

Suppose they are 5 grm., 500 mg., 200 mg., and 10 mg.

The weight of the watch-glass = 5·00 grm.

	·50 grm.
	·20 grm.
	·01 grm.
Total	5·71 grm.

Replace the weights in the box and check the weight by noting the value of each weight as you do so. For the first few lessons it is advisable to write down the value in grammes of each weight, and then total them as in the example above. After a little practice you will be able to write down the total weight without this addition.

Find in a similar manner the weight of a crucible and lid (fig. 23 C), and the weight of an evaporating dish (fig. 7).

Apparatus for Heating Substances.

(a) *The Bunsen Burner* (fig. 3).—This is the chief apparatus used for heating in a laboratory where gas is available.

The gas enters the burner through the pipe G (fig. 3), and mixes with air which enters through the air-hole A. The mixture of gas and air burns at F with a very hot blue flame. By mixing air with the gas in this way the gas is more fully consumed, and the flame is much hotter than a flame of gas alone. Because the gas is more thoroughly consumed the flame gives out very little light—we say it is non-luminous.
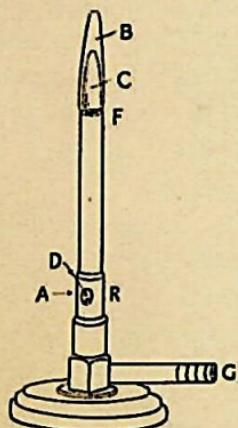
The ring R can be turned round to alter the size of the air hole, and thus alter the amount of air admitted. After the burner has been lighted, the size of the air-hole should be altered until the gas burns quietly. If the air-hole is too large the flame will make a "roaring" noise. Light the Bunsen burner and notice that the flame consists of two cones of flame B, C. The hottest part of the flame is just above the tip of the inner cone C. If you lessen the supply of gas to the burner the flame gets smaller and smaller, and at last the gas ceases to burn at F and begins to burn at D. When this happens, the burner is said to have "struck back". Whenever the burner "strikes back" the gas should be turned out *at once* and relit, because a poisonous gas is formed when the gas is burning at D.

Fig. 3.—Bunsen Burner
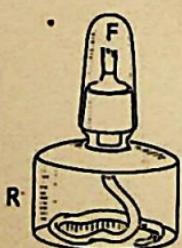
Fig. 4.—Spirit-lamp

(b) *The Spirit-lamp* (fig. 4).—This source of heat usually consists of a glass or metal vessel R (fig. 4) containing methylated spirits. The methylated spirit rises through small holes in the threads of which the wick is composed, and burns at F with a hot, non-luminous flame.

This method of heating is only used where gas is not avail-

able. The flame of the spirit-lamp is not as hot as the flame of the Bunsen burner. For experiments which require a flame hotter than the flame of the spirit-lamp or the Bunsen burner a fire or furnace of some kind must be used.

Experiment 4.—To find the weight of 1 cu. cm. of water.

Obtain a beaker (fig. 6) and weigh it. Place 10 cu. cm. of water in it. The water may be measured by means of a 10-cu.-cm. pipette (fig. 5).

Place the end B of the pipette well below the surface of the water contained in a second beaker. Place the end C in the mouth and suck out the air from inside the pipette. This will cause the water to rise in the pipette. Continue the suction until the liquid rises just above the mark A.[1] Then quickly remove the end C from the mouth, and close C by means of the finger tip. If the liquid surface falls below A, the operation must be repeated. By cautiously raising the finger which closes the end C, when the water surface is above A, it is possible to let the water escape at B until the lowest part of the curved surface of the water (the meniscus) reaches A.

Hold the pipette over the weighed beaker, and on removing the finger from C the pipette will deliver 10 cu. cm. of water.

Fig. 5.—
Safety
Pipette

Weigh the beaker and its contents.

The increase in weight is the weight of 10 cu. cm. of water. Calculate the weight of 1 cu. cm. of water.
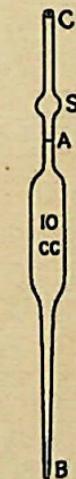
[1] Be very careful or you may draw the liquid up into your mouth. By attending carefully to what you are doing this will never happen, unless there is insufficient liquid in the beaker to fill the pipette.

With dangerous liquids it is advisable to use a safety pipette. The bulb at S (fig. 5) renders it next to impossible to get any of the liquid into the mouth accidentally.

CHAPTER II

SOLUTION

Experiment 5.—To find the action of water upon certain solids.

Use common salt, sand, sugar, and copper sulphate.

Place a little of the substance, which should be in the form of a powder, in a clean beaker (fig. 6). Add to it about 25 cu. cm. of water.[1]

Fig. 6.—Beaker and Stirring-rod

Stir the substance and water by means of a piece of glass rod with a short piece of rubber tubing on one end, called a stirring rod. The rubber end will save the beaker from breakage when the liquid is stirred. Allow the mixture of substance and water to stand for about five minutes, stirring it occasionally. This will allow the water a better opportunity to act upon the salt. Then carefully examine the mixture.

Can you now see any of the particles of substance which were added to the water? If there are no particles of the substance visible we say the substance has completely *dissolved* in the water. It may be that there are *some* particles of the substance visible, but not as much as you placed in the beaker. This indicates that the substance has partly dissolved.

Possibly it may not be easy to decide with certainty whether any of the substance has dissolved or not. In this case the contents of the beaker must be undisturbed until the solid has settled to the bottom of the beaker, and the liquid above it is perfectly clear. When there are no particles of the substance floating about in the liquid, pour some of the clear

[1] Distilled water should be used for this and for the succeeding experiments on solution, especially if the tap-water available is very hard.[1]

liquid down the stirring-rod (fig. 7) into a clean evaporating-dish, without disturbing the solid at the bottom of the beaker.

(This process is spoken of as *decantation*, and the liquid is said to have been de-canted.)

Place the evaporating-dish, containing the de-canted liquid, on a wire gauze upon a tripod (fig. 8), and place the lighted Bunsen burner under-neath. When nearly all the water has boiled away remove the flame from under the evaporating-dish, and only replace it

Fig. 7.—Decantation

for a few seconds now and then so as to just keep the liquid boiling. By so doing you will be able to drive off the whole of the water, and leave behind any solid which was in solution in the water. This process is spoken of as evaporating to dryness. If on evaporating to dryness there is no solid left in the evaporating-dish, it indicates that the substance was insoluble in water.

Experiment 6.—To find whether more of a given substance will dissolve in hot water than will dissolve in an equal weight of cold water.

Into a beaker place about 25 cu. cm. of water. Add potas-

Fig. 8.—Evaporation

sium nitrate to the water little by little, stirring after each addition. At first the substance will dissolve on stirring. After about 7 or 8 grm. of the potassium nitrate have been added, however, it will be found that some of the substance
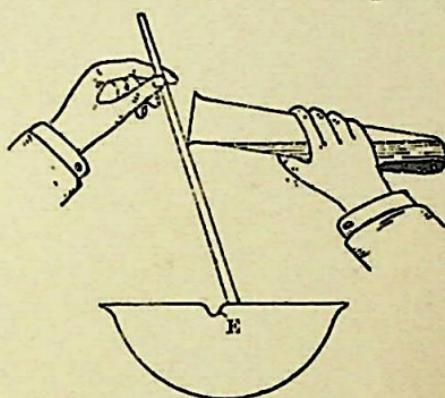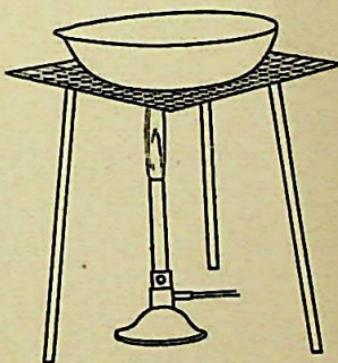
will remain undissolved at the bottom of the beaker. This indicates that the water has dissolved as much potassium nitrate as it can dissolve at that temperature. The solution is said to be a *saturated* solution of potassium nitrate.

Now place the beaker on a wire gauze supported on a tripod. Warm the saturated solution gently by means of a Bunsen burner. Stir the solution while warming it.

Does the undissolved potassium nitrate dissolve on warming the solution? If so, add a little more potassium nitrate and stir the solution again.

Does *this* potassium nitrate also dissolve?

Repeat the experiment, using the following substances:— Sodium sulphate, potassium chlorate, alum, and common salt.

Are the substances tested more soluble in hot than in cold water?

It has been found from the results of experiments, similar to those just performed, that salt and sugar are soluble in water, and give a colourless solution. Copper sulphate dissolves in water, giving a blue solution. Sand is insoluble in water.

A substance is said *to dissolve* in water when it forms a solution with the water.

A *solution* of a substance in water is a mixture of that substance with water, which appears to be perfectly clear, and from which the substance cannot be separated by decantation nor by filtration (see also p. 240).

The dissolved substance is spoken of as the *solute*; the liquid in which the substance dissolves is the *solvent*; the mixture of solvent and solute is the *solution*.

If a large amount of potassium nitrate is added to some water, the substance gradually dissolves. The potassium nitrate continues to pass into solution until *a definite amount* has dissolved. Any potassium nitrate in excess of this amount remains undissolved. The solution is then said to be *saturated*.

A *saturated solution* is one which can exist unchanged in the presence of the solute; that is, when the substance is in con-

tact with its *saturated* solution the substance does not dissolve; neither does any of the substance come out of solution.

Experiment 7.—To measure the temperature of certain bodies.

To measure how hot a body is, or, in scientific language, to measure the temperature of a body, a thermometer (fig. 9) will be necessary.

The usual form consists of a tube T (fig. 9), with a bulb B at the end. The bulb and part of the tube are filled with mercury. When the thermometer is made warmer the mercury in it expands (increases in volume) and so reaches a point higher up the tube. As the mercury cools it decreases in size (contracts) and so does not reach so far up the tube. Thus the height up the tube of the top of the mercury column indicates the hotness or temperature of the substance in which the bulb of the thermometer is placed.

If the substance is as hot (or cold) as melting ice the mercury reaches the part of the tube level with the line marked 0 on the scale s, and the temperature is said to be 0 degrees centigrade. If the substance is as hot as the steam from water boiling under normal atmospheric pressure, the mercury will reach the part of the tube level with 100, and the temperature is said to be 100 degrees centigrade. When the bulb of the thermometer is placed in a substance, if the mercury rises to 30 on the scale, the temperature of the substance is 30 degrees centigrade, written 30° C. [What temperature is indicated by the thermometer in fig. 9?]

Fig. 9.—Centigrade Thermometer

(i) Hang up the thermometer in the laboratory. In a few minutes the mercury will reach the temperature of the room. Then note the reading of the thermometer. This is the temperature of the air at that place.

(ii) Fill a beaker with water freshly drawn from the tap.

Place the thermometer in the beaker of water. When the mercury in the tube ceases to move, note the temperature. [Is the temperature of the water above or below that of the air?]

(iii) Heat the water in the beaker by means of a Bunsen burner, and take the temperature of the water every minute. Continue the operation until the water has been boiling for a few minutes.

State what you notice about the temperature changes (a) before the water boils, (b) after the water boils.

Experiment 8.—To find the strength of a solution.

Take about 30 cu. cm. of water in a beaker and add salt to the water, stirring meanwhile, until a layer of salt remains undissolved at the bottom of the beaker. Allow the solution to stand for ten minutes, stirring it occasionally, and if there is still some salt remaining at the bottom of the beaker we may assume that the solution is a saturated one. Place a thermometer in the liquid in the beaker. While the solution is standing, weigh a clean, dry evaporating-dish [1] [weight = a grm.].

Observe the reading of the thermometer, and write down the temperature of the solution. Then put away the thermometer in its case.

Decant the clear solution into another beaker, and withdraw 10 cu. cm. of the solution by means of a pipette. Allow this solution to run out of the pipette into the weighed evaporating-dish. Weigh the dish and its contents (weight = b grm.). By subtraction obtain the weight of the solution [weight = $(b - a)$ grm.].

Place the evaporating-dish on a beaker half full of water. Arrange the beaker, gauze, and tripod as in the diagram (fig. 10). [Such an arrangement makes a simple form of *steam bath.*]

Boil the water in the beaker by means of the Bunsen burner. The steam escapes from the spout of the beaker after heating the evaporating-dish.

[1] Read again the rules on weighing given in p. 4.

[If the Bunsen burner, instead of a steam bath, is used to heat the solution, the rapid heating which occurs causes particles of salt to be shot out of the evaporating-dish.]

Evaporate the solution in the evaporating-dish to dryness, that is until no more water can be driven off. Then dry the outside of the evaporating-dish, and weigh it and the contained salt when it has cooled (weight = c grm.). Obtain by subtraction the weight of salt and also the weight of water driven off.

Fig. 10.—Evaporation on Steam Bath

Calculate the weight of salt which can be dissolved by 100 grm. of water at the temperature of the laboratory, as in the example below.

Example—

				Temperature	=	15° C.	
Weight of evaporating-dish					=	21·22 grm.	(a).
,,	,,	,,	+ solution		=	34·45 ,,	(b).
,,	,,	,,	+ salt		=	24·45 ,,	(c).
,,	salt				=	3·23 ,,	$(c-a)$.
,,	water				=	10 ,,	$(b-c)$.

$(b-c)$ grm. of water at 15° C. will dissolve $(c-a)$ grm. of salt.

∴ 100 grm. of water at 15° C. will dissolve

$$\frac{(c-a)}{(b-c)} \times 100 \text{ grm. of salt.}$$

Then 10 grm. of water at 15° C. will dissolve 3·23 grm. of salt.

∴ 100 grm. ,, ,, ,, 32·3 ,, ,,

or, 100 cu. cm. ,, ,, ,, 32·3 ,, ,,

since 1 cu. cm. of water at 15° C. weighs almost exactly 1 grm.

Solubility.—*The weight of salt that can be dissolved by 100 cu. cm. of the solvent to make a saturated solution at a certain temperature is called the solubility of the salt at that temperature.*

As we have seen, the solubility depends upon the temperature, and therefore in stating the solubility of a substance the temperature must always be specified.

The solubility of common salt at 0° C. = 35·63.

This means that at a temperature of 0° C. 100 cu. cm. of pure water will dissolve 35·63 grm. of common salt to form a saturated solution.

The solubility of potassium nitrate at various temperatures is given below.

Temperature	0°	10°	20°	30°	40°	50°	C.
Solubility ...	13·3	20·9	31·6	45·8	63·9	85·5	grm.

The information contained in this table is seen much more quickly and with less effort if the relation between the numbers is shown graphically, as in fig. 11. We will now proceed to represent the relation between the temperature and solubility of potassium nitrate graphically.

To draw the solubility curve for potassium nitrate from the figures given above.

Use a sheet of paper ruled in half-inch or other suitable squares.

On it draw two lines A B and B C at right angles to one another, as in the diagram fig. 11. Along A B write "solubility", and along B C write "temperature". Let each space measured to the right of A B represent an increase of temperature of 5° C., and let each space measured above B C represent 10 grm. Number the spaces along A B and B C in accordance with this agreement (fig. 11).

From the figures given, the solubility of potassium nitrate at 50° C. = 85·5 grm. Mark D at 85·5 grm. and E at 50° C. Find where the lines D F and E F meet at F. The point F should be marked with a small cross. F is one point on the curve to be drawn, which is called a graph. By proceeding in a similar manner for the other solubilities given we obtain points G, H, I, J, K. Draw a smooth curve evenly amongst
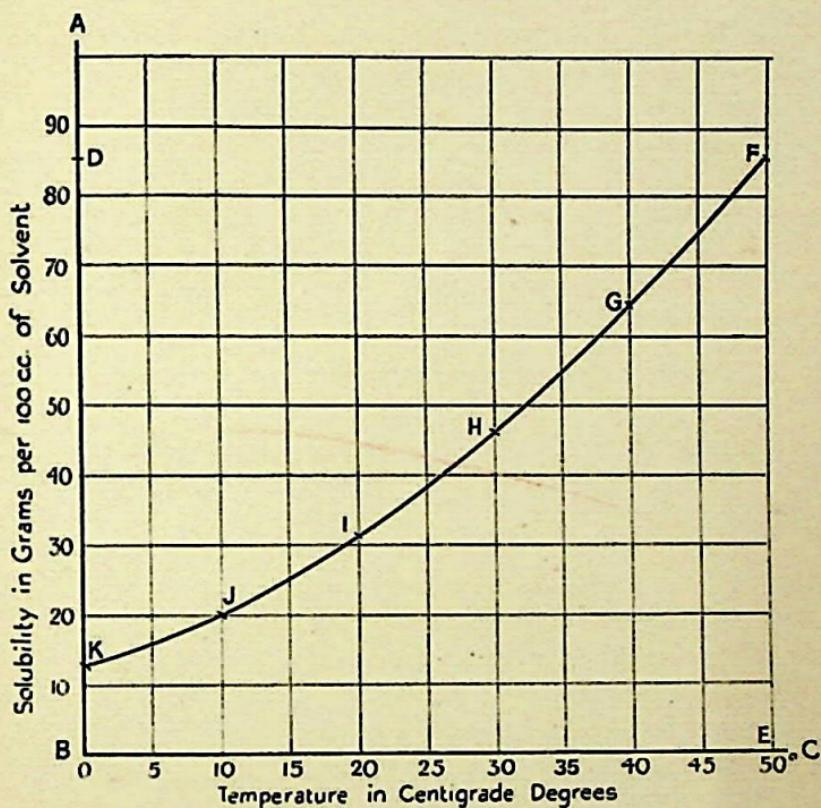
Fig. 11.--Solubility Curve for Potassium Nitrate

the points, and the graph expressing the solubility of potassium nitrate is complete.

In a similar manner, and on the same page, plot the solubility curves for potassium chlorate and common salt from the data supplied below.

Temperature in degrees centigrade	0°	10°	20°	30°	40°	50°	
Solubility of potassium chloride	27·6	31·0	34·0	37·0	40·0	42·6	grm.
Solubility of common salt	35·7	35·8	36·0	36·3	36·6	37·0	grm.

What the solubility curve indicates

By observation of the curves just drawn obtain answers to the following questions:—
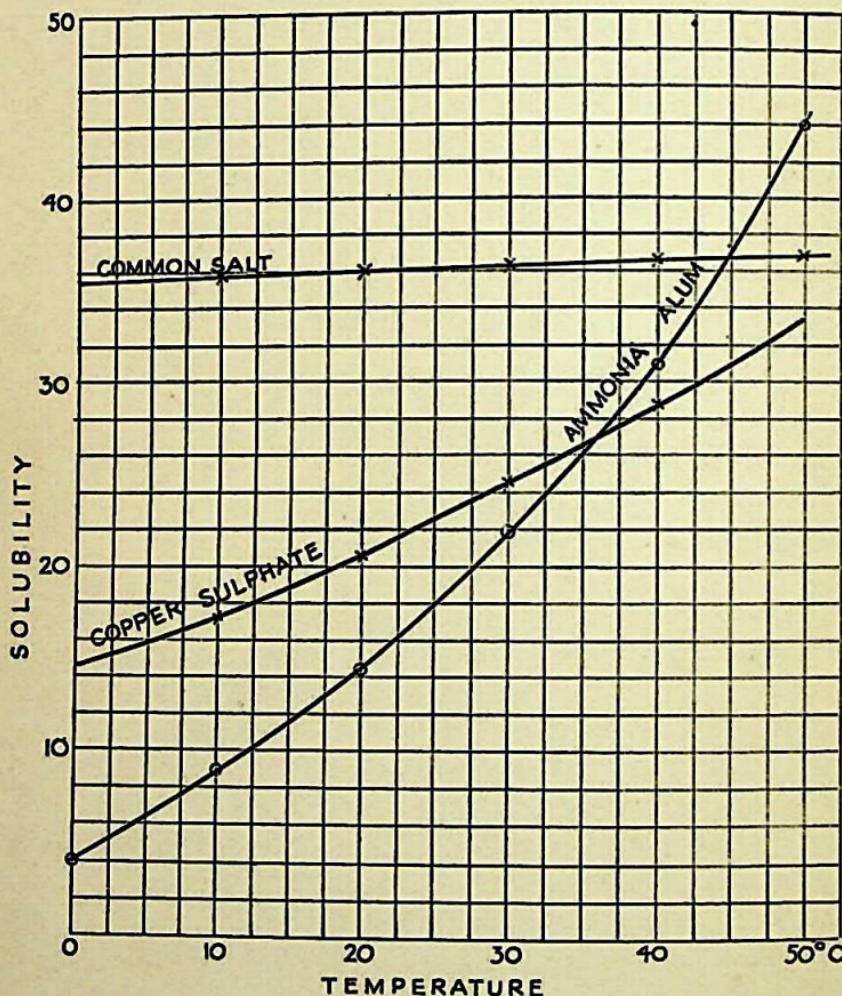
Fig. 11A.—Solubility Curves

1. By what percentage does the solubility of potassium nitrate change between (*a*) 0° C. and 25° C.? (*b*) 25° C. and 50° C.?

2. What is the solubility of potassium nitrate at 25° C.? [On the graph (fig. 11) find 25° C. Look along the vertical line through 25° C., and from where it meets the curve look

along the horizontal line until the line A B is reached.   The solubility at 25° C. is given by the number on A B where this horizontal line cuts A B.]

3. At what temperature have common salt and potassium nitrate the same solubility ? [Plot on the same paper and find where the curves for common salt and potassium nitrate cut one another.   From the point of intersection draw a vertical line to meet B C.]

Experiment 9.—To find the solubility of potassium chlorate at various temperatures, and to draw the solubility curve for the substance.

[In performing this experiment each student should find the solubility for a different temperature, not exceeding 50° C., and the class results should be collected and graphed by each member of the class.]

Obtain a clean, dry evaporating-dish, and find its weight.

· Fit up the apparatus shown in the diagram (fig. 12).   B is a beaker nearly full of water.   S is a test-tube also nearly full of water.   T is a thermometer.   W is a wire gauze.

Place sufficient potassium chlorate in the water in the test-tube to saturate the water at the required temperature, and to leave a layer of undissolved potassium chlorate at the bottom of the test-tube.

Fig. 12.—Preparation of a Saturated Solution at a given Temperature

S, Test-tube containing saturated solution.   T, Thermometer.

Heat the water in the beaker to the required temperature - by means of a Bunsen burner, stirring the water occasionally. Try to keep the water at this temperature for ten minutes by removing or replacing the Bunsen burner as required.   Meanwhile the solution in the test-tube should be stirred by means of a stirring-rod to ensure that it is saturated.

Warm a 10 cu. cm. pipette by filling it with water from B.

(C 729)   3

[A cold pipette would cool the solution, and probably cause some of the dissolved solid to be deposited in the pipette.]

See that the pipette is quite empty, and then withdraw 10 cu. cm. of the solution from the test-tube. Transfer it to the weighed evaporating-dish. Evaporate the solution to dryness on a steam-bath. Then weigh the evaporating-dish and its contents.

The increase in weight of the evaporating-dish gives the weight of potassium chlorate dissolved in 10 cu. cm. of water. Calculate the weight of potassium chlorate which would be dissolved by 100 cu. cm. of water.

Enter your result and the results obtained by the other members of the class in a table similar to that on p. 14. Draw a graph of the results, proceeding as directed on p. 14.

We have seen that substances which are dissolved can be obtained from the liquid by evaporating to dryness; the liquid is driven off as vapour and the substance remains.

We have next to consider how to remove from a liquid, substances which are *only suspended* in the liquid—not dissolved in it. We have previously waited until such insoluble substances have settled down to the bottom of the vessel, and then decanted the clear liquid. It is sometimes a long process to wait until this happens, and a much quicker and also more effective way is to proceed as follows.

Experiment 10.—To free water from suspended impurities.

Use a mixture of tap-water and soil, or other turbid water.

Select a glass funnel (B fig. 13) and a circular filter-paper (*a*). [Filter-paper is a porous paper like blotting-paper.] Fold the paper into halves (*b*), and then into quarters (*c*). Then open it out so that it forms a cone (A).

Fit the filter-paper into the funnel as in B, and arrange the funnel and the remainder of the apparatus as in F.

Take the vessel containing the water with the suspended matter in it, and carefully pour the liquid down the stirring-rod (see fig. 7) into the funnel. The water should not be

allowed to rise above the top of the filter-paper, or the impure
water will escape between the filter-paper and the funnel into
the beaker intended to collect the pure water.

When the substance in suspension in the water is in very
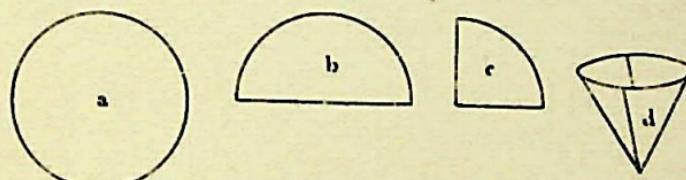
a, Circular filter paper.   b, Same, folded once.   c, Same, folded twice.
d, Opened out into cone.
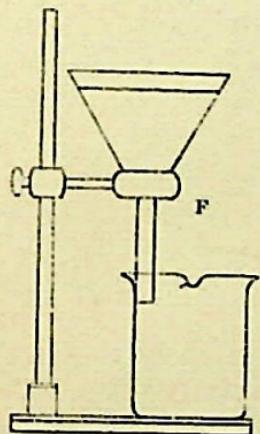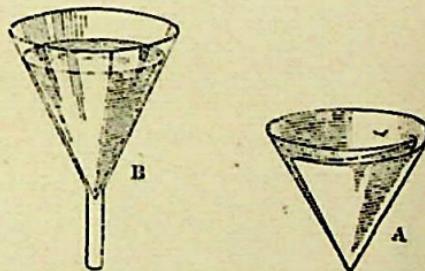
A, Filter-paper folded into proper shape.
B, Filter-paper placed inside glass funnel.

Funnel and Filter Stand

Fig. 13.—FILTRATION

fine particles it may be necessary to pass the filtered liquid
again through the same filter-paper.

Note that the operation just performed, called *filtration*,
removes only suspended matters and not dissolved substances
(see pp. 10 and 240).

The liquid which passes through the filter is called the
filtrate, and the substance remaining on the filter-paper is the
residue.

The Wash-bottle (fig. 14).—A wash-bottle is a piece of
apparatus from which a suitable stream of water may be
obtained for the purpose of washing residues after filtration.

It consists of a flask D (500 cu. cm.) fitted with a stopper pierced by two holes. The stopper is fitted with a piece of bent-glass tube C, one end of which reaches nearly to the bottom of the flask. To the other end of C is attached, by means of a piece of rubber tube, a short piece of glass tube drawn out to a point F. Through the other hole in the stopper passes a bent piece of glass tube A, which projects only a little way into the flask.

Fig. 14.—Wash-bottle

By placing the end of A in the mouth and blowing into the flask, a thin stream of water is forced out of F. The rubber connection allows F to be moved so as to direct the stream of water as required. If a more plentiful supply of water is desired, it can be obtained from A by simply inverting the flask.

Experiment 11.—To find the percentage composition of a mixture of a soluble and an insoluble substance.

Use a mixture of sand and salt. Weigh a small empty beaker. Place about 2 grm. of the mixture in the beaker, and weigh the beaker and its contents. Find by subtraction the weight of the mixture taken. Add to the mixture in the beaker about 5 cu. cm. of water from the wash-bottle. Weigh a clean, dry evaporating-dish, and arrange it and the remainder of the apparatus as shown in fig. 15. Stir the liquid in the beaker and pour it down the stirring-rod into the centre of a filter-paper placed in the funnel. Wait until the whole of the liquid has filtered through into the evaporating-dish. Then, by means of the wash-bottle, direct a fine stream of water on to any solid left in the beaker, holding the beaker in such a way that every particle of the solid in it is washed into the filter-paper. Use as little water as you can to accomplish this.
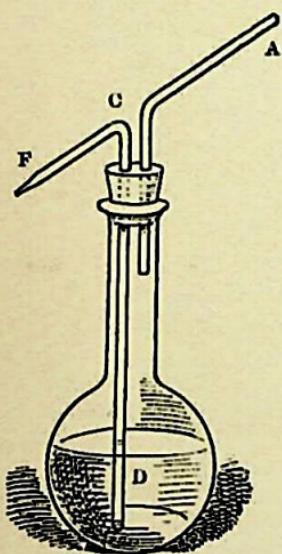
All the sand in the mixture taken will now be on the filter-paper. Most of the salt will be in solution in the water in the evaporating-dish. A little of the salt may be still amongst the sand. To remove this salt from the sand, a fine stream of water should be directed on to the sides of the filter-paper in order to wash the sand into the bottom of the filter-paper and dissolve out any salt still remaining.

[Avoid filling the filter-paper more than half full of water, and avoid using so much water that the evaporating-dish is more than
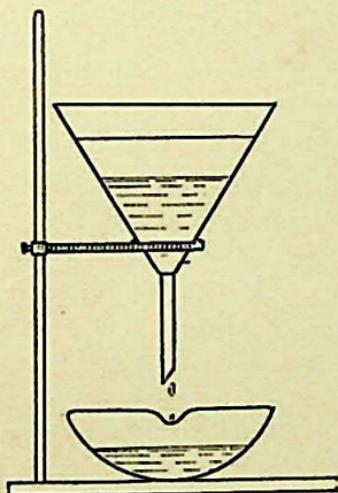
Fig. 15.—Separation of Sand and Salt. Filtration
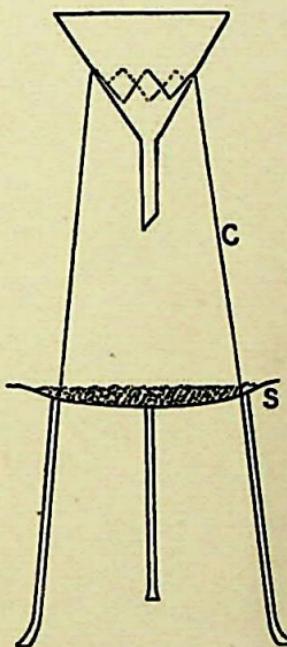
Fig. 16.—Drying the Filter-paper and its Contents

s, Sand-bath. c, Drying cone.

three-quarters full. On the other hand, sufficient water to wash out *all* the salt must be employed. Both these conditions cannot be observed if too much of the mixture be taken.]

Evaporate the solution in the evaporating-dish to dryness on a water-bath, and obtain the weight of salt in the mixture.

To dry the sand[1] place the funnel and its contents in the

[1] To obtain the percentage composition of the mixture, the weight of sand *or* salt only need have been obtained. The percentage of each has been found in this experiment as an indication to the student of the degree of accuracy obtainable by him in the determination.

open end of a tin can (fig. 16). Place this tin can on a sand bath, and place a lighted Bunsen burner underneath. (Such an arrangement constitutes a simple form of air-oven.)

When the sand is quite dry it will easily leave the paper, and may be emptied into a weighed watch-glass or small beaker, and its weight determined.

The weight of mixture taken should be equal to the weight of the sand + the weight of the salt. The nearness with which your results approximate to this is a measure of the accuracy of your work.

Calculate the percentage of salt and sand in the mixture as in the example below.

Example—

Weight of beaker						=	39·50	grm.
"	"	"	+ mixture			=	40·80	"
"	"	mixture				=	1·30	"
"	"	evaporating-dish				=	44·08	"
"	"	"	"	+ salt		=	44·57	"
"	"	salt				=	·49	"
"	"	beaker				=	39·50	"
"	"	"	+ sand			=	40·27	"
"	"	sand				=	·77	"
"	"	mixture				=	1·30	"
"	"	sand + salt				=	1·26	"
				Error		=	·04	"

Percentage of salt in the mixture $= \dfrac{·49}{1·30} \times 100 = 37·7\%$

"   " sand "   " $= \dfrac{·77}{1·30} \times 100 = 59·2\%$

Error $= 3\%$.

In all solutions considered so far the solvent has been water. Water will dissolve a very large number of substances, and so has been called the "universal solvent".

When a substance is described as insoluble, what is usually meant is that it is not soluble in water. Many substances which are insoluble in water are soluble in other liquids.

Experiment 12.—To show that sulphur will dissolve in carbon bisulphide.

This experiment is rather dangerous. This is due to the fact that carbon bisulphide is very inflammable.

Shake up a little powdered sulphur in a test-tube with about 1 cu. cm. of carbon bisulphide.

[*Do not warm the mixture and do not work near a flame, as the vapour of carbon bisulphide very easily catches fire.*]

Filter off any undissolved sulphur. Place the vessel containing the filtrate either in a fume chamber or in the open air, as carbon bisulphide is very poisonous. In a short time the carbon bisulphide will have evaporated, and pieces of sulphur will be left. Make a sketch of one of the pieces of sulphur obtained.

It has just been seen that sulphur will dissolve in carbon bisulphide. Similarly—

Indiarubber is soluble in benzene, ether, or turpentine.
Paraffin   „   „   carbon bisulphide or turpentine.
Iodine   „   „   carbon bisulphide.
Resin   „   „   alcohol.

Several of these solvents are in everyday use—

Alcohol is used as a solvent in varnishes.
Benzene is used as a solvent for rubber, the solution being used for repairing rubber goods.

Experiment 13.—Sublimation.

Select two watch-glasses of the same size and fit them together, one on top of the other, with their edges in contact. Place a little ammonium chloride between the watch-glasses and stand them on a sand-bath. Observe what happens to the ammonium chloride as the sand-bath is heated.

When a substance on heating changes directly into a vapour without first melting it is said to *sublime.*

In the experiment just performed the ammonium chloride sublimed, and the vapour was condensed as a white powder on the upper watch-glass.

Similarly, bottles containing camphor usually have crystals of camphor on the sides of the bottle. The camphor sublimes and is deposited on the cooler portions of the bottle. Sublimation also occurs in a bottle containing iodine.

By sublimation we may effect a separation of two substances one of which is unaffected by heat and the other of which sublimes. (See Experiment 22.)

QUESTIONS ON CHAPTER II

1. How would you decide whether a certain substance was slightly soluble or insoluble in water?

2. Explain the terms "solvent", "solute", and "solution"; "filtration" and "filtrate".

3. How may an unsaturated solution be changed into a saturated one? (Give two methods.)

4. How many grammes of common salt can be dissolved in 10 cu. cm. of ice-cold water? [The solubility of common salt at 0° C. = 35.63.]

5. Obtain from fig. 11 A the solubility of—

        (a) Copper sulphate at 15° C.

        (b) Ammonia alum at 25° C.

        (c) Common salt at 35° C.

6. Plot the solubility curve for iron sulphate from the following figures, and from your graph find the solubility at 40° C.:—

Temperature ...	0° C.	10° C.	30° C.	50° C.
Solubility ...	15.6	20.8	33	48.5

7. How would you proceed to separate potassium nitrate and carbon (charcoal) from a mixture of these substances?

8. Classify the following substances as (a) very soluble, (b) soluble, (c) insoluble or slightly soluble: potassium nitrate, sand, chalk, sugar, alum, lime.

9. Name three common solvents, and in each case give two substances which they will dissolve.

10. How would you proceed to show that the solubility of common salt is almost the same at all temperatures up to 100° C.

CHAPTER III

DISTILLATION AND CRYSTALLIZATION

Distillation.—To obtain the *solid* from its solution the liquid has hitherto been driven off into the air in the form of vapour by boiling the solution.

If it is the *liquid* that we desire to obtain, means must be taken to cool the escaping vapour until it condenses, that is,
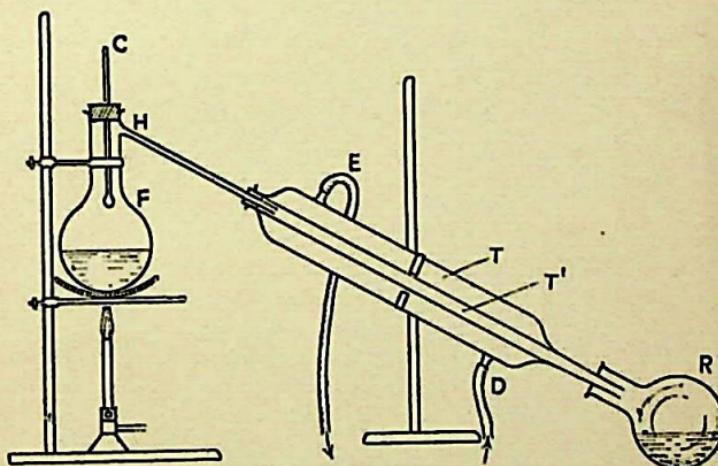
Fig. 17.—Distillation

changes again to a liquid, and to collect the condensed liquid. The process of changing a liquid to a vapour by means of heat, and then condensing the vapour by cooling it, is spoken of as *distillation*.

The apparatus used is called a *condenser*. The form of condenser illustrated in fig. 17 was devised by Liebig, and is called a Liebig's condenser. It consists of an outer tube T and an inner tube T'. The tube T' is kept cool by a stream of cold

water, which, entering at D, flows *up* to E, and thence to the sink.

The liquid to be distilled is placed in a distilling-flask F, fitted with a stopper, through which passes a thermometer C. The distilling-flask has a side-tube H which passes through a stopper in one end of the tube T′ of the condenser. The other end of T′ passes into a suitable flask R, called the *receiver*. When the liquid in F is boiled it changes into vapour, which passes through the inner tube T′. On its way the vapour is
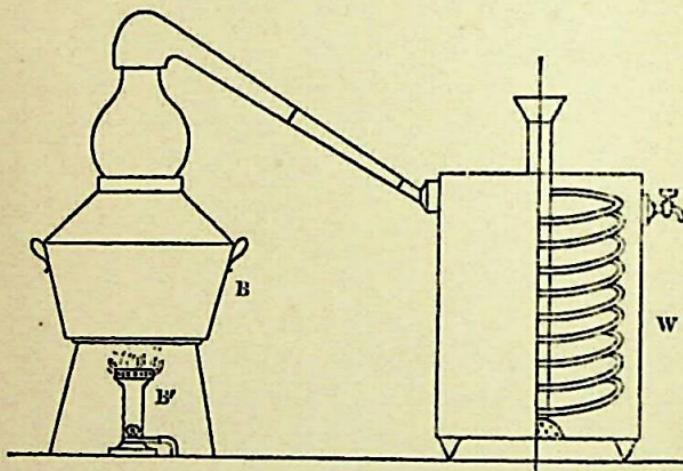
Fig. 18.—Still for preparing Distilled Water

B, Boiler. W, Worm of block-tin surrounded by cold water. B′, Rose burner for heating the water.

cooled by the cold water flowing through T. This cooling condenses the vapour, and the liquid formed drips from the end of T′ into the receiver.

Another form of distilling apparatus suitable for preparing distilled water for use in the laboratory is illustrated in fig. 18. The water is boiled in B, and its vapour, passing through the coil of block-tin tubing W, immersed in cold water, is condensed.

Experiment 14.—To obtain pure water from water containing dissolved and suspended impurities.

Use water containing copper sulphate and soil.

Fit up the apparatus shown in fig. 17. Half fill the flask F

with the impure water. Insert the stopper and thermometer
c, so that the bulb of the thermometer does not touch the
liquid. Boil the liquid in F, and collect the distillate in the
receiver R. Notice the temperature of the vapour as indicated
by the thermometer. When a few cubic centimetres of water
have collected, empty this water away and replace the receiver
R. This water will probably not be very pure, because im-
purities in the water may have distilled over. Collect as
much of the distilled water as is required. Does the distilled
water contain—(a) Any suspended substances? (b) Any dis-
solved substances?

[Evaporate some of the distilled water to dryness on a
watch-glass.]

Note that the temperature of the vapour during distillation
was steady at about 100° C.—the boiling-point of pure water.

Similarly if alcohol is distilled, the temperature of the
vapour is steady at 78° C.—the boiling-point of alcohol.

Experiment 15.—To separate a liquid from its solution in another liquid.

Use a mixture of alcohol and water.

Use the same apparatus as in the last experiment. Place
the mixture in F (fig. 17) and boil it gently. Notice the
thermometer reading throughout the experiment. ˙

Collect the first portion of the distillate in R.   This is
mainly *alcohol.* Call it "A".

When the thermometer rises above about 80° C. remove R
and put another receiver in its place. Distil about one-half of
the liquid remaining in F. This will be a mixture of *alcohol
and water.* The liquid left in F will be mainly *water.* Empty
the flask F and redistil the first portion of the distillate "A".
Collect only the portion which distils while the thermometer
indicates 78° C. This redistilled alcohol will be purer than
"A". If necessary it may be again distilled, and in this way
very pure alcohol will be obtained. This process is spoken of
as *fractional distillation.*

In the manufacture of spirits, alcohol is separated from the
fermented liquor, in which it is made, by distillation.

Crystals and Crystallization.—On referring to the solubility curve for alum it is seen that 100 cu. cm. of water at 25° C. is able to dissolve 18 grm. of alum; but that the same amount of water at 20° C. is saturated when it contains 14 grm. of alum.

If, then, a saturated solution of alum be made in water at 25° C., and allowed to cool to 20° C., $(18 - 14) = 4$ grm. of alum should separate out from the solution. Let us observe in what *form* it separates out.

Experiment 16.—(i) To crystallize ammonia alum.
Into an evaporating-dish place about 10 cu. cm. of water, and add to it about 10 grm. of ammonia alum.

Place the evaporating-dish on a wire gauze placed upon a tripod, and warm the solution until the alum is dissolved. Place the evaporating-dish containing the warm solution aside and allow it to cool. When the contents are cool, notice the regular-shaped pieces of alum (*crystals*) which have been deposited on the bottom of the dish. Place several of the largest of the alum crystals on a piece of filter-paper to dry them. Separate and carefully examine the dry crystals. Try to answer the following questions:—

  (*a*) Have all the crystals the same number of faces?
  (*b*) Are the corresponding faces on the crystals the same shape?
  (*c*) Are the faces flat or curved surfaces?

Make a drawing of the crystal which you consider to be the most perfect in shape.

(ii) To crystallize copper sulphate.
Proceed exactly as in (i). Use about 10 grm. of copper sulphate in place of the alum. Answer questions (*a*), (*b*), and (*c*), and make a sketch of one of the crystals.

Crystalline and Amorphous Bodies.—When a saturated solution of copper sulphate or alum is allowed to evaporate, and so has some of the water removed, part of the solid separates out from the solution. The same thing happens if

the solution is cooled to such an extent that the amount of solid present in the solution is more than enough to saturate it.

The pieces of solid deposited differ from, say, pieces of broken glass in several respects. The most noticeable though not the most important difference is the definite geometrical shape and flat faces of the particles. Such particles are called *crystals*. Substances which are not crystalline are spoken of as *amorphous bodies*.

Distorted Crystals.—Crystals, whether grown in the laboratory or formed in nature, are seldom, if ever, perfect. This is due to the fact that the crystal does not grow equally in all directions. This irregular growth may be due to the fact that the concentration of the solution is not the same all round the crystal; also the bottom of the containing vessel and neighbouring crystals interfere with the growth of the crystal.

If the solution is cooled slowly the crystals formed are usually larger than when it is cooled rapidly. The best position for crystal growth is when the crystal is suspended in the solution.

Experiment 17.—To grow a crystal of copper sulphate.

Select one of the largest crystals
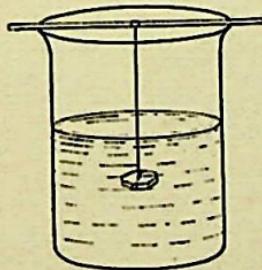
Fig. 19.—Growth of a Crystal
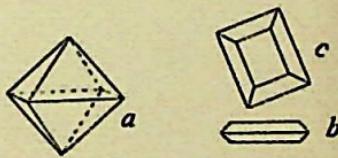
Fig. 20.—Crystals

a, Crystal of alum. *b*, *c*, Crystals of sugar.

from those already made in Experiment 16. Hang it by means of a thread in a cold saturated solution of copper sulphate contained in a clean beaker (fig. 19). Place the beaker aside for some weeks, and copper sulphate from the solution will be deposited on the crystal as the liquid slowly evaporates.

Sketches of crystals of various substances are given in fig. 20.

Mechanical Processes of Separation.—In this chapter and the previous one the following methods have been used to separate substances which have been mixed:—

1. *Solution.*	3. *Crystallization.*
2. *Distillation.*	4. *Sublimation.*

The following methods of separation are useful in some cases:—

5. Removal of magnetic particles, such as iron, by means of a *magnet.*

6. Separation of light and heavy particles by *washing* the light particles out of the mixture. This is the method adopted to separate the heavy gold-dust from the lighter quartz particles in gold-mining. In the winnowing of grain the lighter husk is blown away, leaving the heavier grain.

These six methods are spoken of as *mechanical processes* of separation. The difference between these mechanical processes and *chemical* processes will be understood after reading Chapter VIII.

WATER OF CRYSTALLIZATION

Experiment 18.—To find the effect of heat upon crystals of copper sulphate.

Place a few dry crystals of copper sulphate in a dry test-tube. Fit the test-tube with a cork and delivery-tube (B, fig. 21). Heat the copper sulphate and collect the liquid given off in an empty flask into which the delivery-tube dips. The test-tube may be held by means of a test-tube holder (A, fig. 21). Continue the heating, moving the Bunsen flame along the test-tube until the crystals turn white.

Remove the stopper and delivery-tube from the test-tube containing the white copper sulphate, and empty out a *little* of the white residue into a watch-glass. Pour a few drops of the liquid collected upon it, and observe that the copper sulphate again turns blue. Add a few drops of water, or turpentine, or oil, or any other liquid available, to another portion

of the white copper sulphate, and observe that only water, or liquids containing water, will restore the blue colour to the white copper sulphate. This seems to indicate that the liquid given off from copper sulphate on heating is water. This water is called *water of crystallization.*
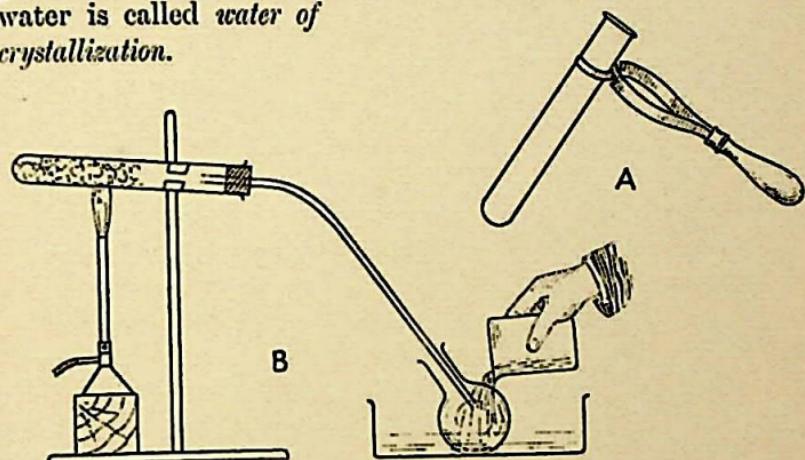
Fig. 21.—A, Test-tube and Holder.   B, Removal of Water of Crystallization from Crystals

Experiment 19.—To determine whether certain crystals contain water of crystallization.

Use alum, potassium sulphate, nitre, and magnesium sulphate.

Heat a few of the crystals of each substance in turn, exactly as in Experiment 18, and collect the liquid, if any.

Make some white copper sulphate by driving off the water of crystallization from a few blue crystals and add a small quantity to the liquid collected. If the blue colour is restored, it may be assumed that the liquid collected is water.[1]

Many crystals, such as magnesium sulphate, zinc sulphate, copper sulphate, and washing-soda contain some water as part of themselves. This water is called water of crystallization. Crystals which do not contain water of crystallization

[1] The restoration of the blue colour to the white copper sulphate only proves that the liquid given off contains *some* water—not that it is water and only water As a matter of fact, the liquid collected is not pure water, for it contains a little dissolved matter.

are said to be *anhydrous*. White copper sulphate is anhydrous copper sulphate. If a crystal of washing-soda which has been exposed to the air be examined, it is seen to be covered with a whitish powder which is very different in appearance from the transparent colourless crystals before exposure. This is due to the fact that the crystal has given up most of its water of crystallization, and so has changed into small crystals containing very little water of crystallization. These are the "whitish powder".

When crystals lose their water of crystallization on exposure to the air they are said to *effloresce*.

Fig. 22.—Drying Tube

Washing-soda and sodium sulphate are efflorescent substances.

Some substances on exposure to the air *absorb* water from the air and become moist, and ultimately dissolve in the water so absorbed. Such substances are said to *deliquesce*. Calcium chloride, zinc chloride, and ferric chloride are deliquescent substances.

Calcium chloride is, for this reason, often used when it is required to remove the moisture from a gas. To dry the gas it is passed through a tube containing anhydrous calcium chloride (fig. 22).

Experiment 20.—To determine the percentage of water of crystallization in some crystals.

Use magnesium sulphate.

Weigh a clean, dry crucible and lid (c, fig. 23).

Into the crucible place about 1 grm. of powdered magnesium sulphate crystals. Place the crucible on a pipe-clay triangle resting on a tripod.[1]

Arrange the lid so that the steam may escape.

Heat the crucible by means of a small flame about 3 cm. below it. Gradually increase the size of the flame.

[1] The crucible may, if desired, be placed on a sand-bath instead of a pipe-clay triangle while being heated.
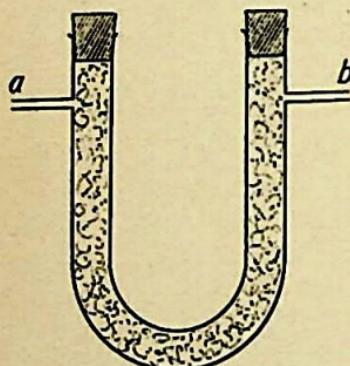
After heating thus for fifteen minutes the crucible and its contents should be allowed to cool and again be weighed.

They should then be replaced on the pipe-clay triangle and heated for another five minutes, after which they should be allowed to cool and be weighed again. If a further loss in weight has occurred, the heating must be repeated until the weight remains constant. It may then be assumed that the whole of the water of crystallization has been driven off.

Fig. 23.—Percentage of Water of Crystallization in Crystals

The percentage loss in weight of the magnesium sulphate on heating should be calculated as in the example below.

Example—

Weight of crucible and lid $= 18 \cdot 34$ grm.

„   „   „ $+ \left\{ \begin{array}{l} \text{magnesium} \\ \text{sulphate} \end{array} \right\}$ (before heating) $= 19 \cdot 00$ „

„   „   „   „   (after heating) $= 18 \cdot 66$ „

Loss in weight $=$ $\cdot 34$ „

$\cdot 66$ grm. of magnesium sulphate on heating loses $\cdot 34$ grm.

$\therefore$ 1 grm.   „   „   „   „   loses $\dfrac{\cdot 34}{\cdot 66}$ „

$\therefore$ 100 grm.   „   „   „   „   loses $\dfrac{\cdot 34}{\cdot 66} \times 100$ grm.

Percentage of water of crystallization in magnesium sulphate $= 51 \cdot 5$.

Experiment 21.—To observe the growth of crystals of nitre (potassium nitrate), common salt (sodium chloride), zinc sulphate, lead nitrate, and ammonium chloride under the microscope.

Make a hot saturated solution of each of the substances

(O 729)   4

mentioned, using a very little water. Place one or two drops of the hot solution on a watch-glass, and as it cools observe the growth of the crystals by means of a convex lens, or a compound microscope if one is available. Seek to be able to identify the substance in future by the appearance of the crystals so formed.

Experiment 22. — To find the percentage of ammonium chloride in a mixture of sand and ammonium chloride.

Weigh out 1 or 2 grm. of the mixture into a weighed crucible, without the lid. Determine the weight of the mixture taken.

Heat the crucible and its contents on a sand-bath until the weight remains constant. The whole of the ammonium chloride will then have been driven off as dense white fumes.

Calculate the percentage loss in weight, which is, of course, the percentage of ammonium chloride in the mixture.

Additional Experiments.—The additional experiments at the end of this chapter are intended to provide experiments for students who, for one reason or another, get the class experiment completed before the remainder of the class.

They are of such a nature that they may be commenced and continued during the odd minutes when the pupil has completed the ordinary class work of the lesson.

Experiment 23.—To grow a large crystal of alum.

Proceed as in Experiment 17, and let the crystal grow for several weeks; then sketch and preserve it.

Experiment 24.—To crystallize ferrous ammonium sulphate.

Make a saturated solution of ferrous ammonium sulphate at about 50° C., and allow it to cool to about 20° C. Then pour off the mother liquor into a crystallizing-dish, and put it away until it crystallizes.

Dry the crystals formed on blotting-paper and preserve them.

Experiment 25. — Determine the percentage of water of crystallization in zinc sulphate crystals.

QUESTIONS ON CHAPTER III

1. How would you prepare pure water from sea-water? Sketch the apparatus you propose to use.

2. Explain the terms: "distillation", "distillate", "vapour", and "evaporate".

3. You are given some powdered alum. Describe exactly how you would proceed to make a large alum crystal.

4. What is meant by "water of crystallization"? How would you determine the percentage of water of crystallization in zinc sulphate?

5. Explain the terms: "anhydrous", "efflorescent", and "deliquescent". Name two examples of each class of substances.

6. How would you proceed to determine whether the gas supply contains water vapour or not?

7. Describe a method of distilling water. What impurities would be removed from the muddy water of a pond (a) by distillation, (b) by filtering? (C. L.)

8. Describe the methods you would adopt to obtain from gunpowder (a mixture of potassium nitrate, carbon, and sulphur) a specimen of each of the constituents in a fairly pure state? (C. L.)

9. Give two examples of the processes of crystallization and distillation as used practically for obtaining substances in a state of purity. (C. L.)

CHAPTER IV

A PRELIMINARY STUDY OF AIR

Has the Air Weight?

To find an answer to this question all that is necessary is to weigh a closed flask from which all the air has been removed, and then to weigh it again when it is full of air.

Experiment 26.—(i) Take a round-bottomed flask having

a capacity of about 500 cu. cm. Place in it about 50 cu. cm. of water. Fit the flask with a rubber stopper and straight glass tube T (fig. 24). Attach a short piece of rubber tubing, R, to the glass tube, and put a screw clip, C, on the rubber tube. Unscrew the clip.

Fix the apparatus on a retort-stand by means of two rings and a piece of wire gauze. By means of a Bunsen burner or spirit-lamp boil the water in the flask. When steam has been coming out of the tube for a few minutes, all the air will have been swept out of the flask by the steam.

Remove the Bunsen burner and quickly screw up the clip to prevent air from entering the flask. Allow the flask and water to cool; then hang the flask, by means of a fine wire W, from the hook of a balance. Weigh the flask. (Weight = a grm.)

Open the clip. (What happens?)

Again weigh the flask and its contents. (Weight = b grm.)

Compare a and b. (Has the air weight?)

Fig. 24.—Weight of a Litre of Air

(ii) **To find the weight of a litre of air.**

Pour the water remaining in the flask used in Experiment 26 (i) into a measuring cylinder and read the volume of the water. (Volume = x cu. cm.)

Fill the flask with water, and by means of a measuring cylinder find how many cubic centimetres of water the flask will hold. (Capacity = y cu. cm.)

The difference between the capacity of the flask and the volume of water remaining in the flask after Experiment 26 (i) will be the volume of air which entered the flask when the clip was opened. [Volume of air = $(y - x)$ cu. cm.]
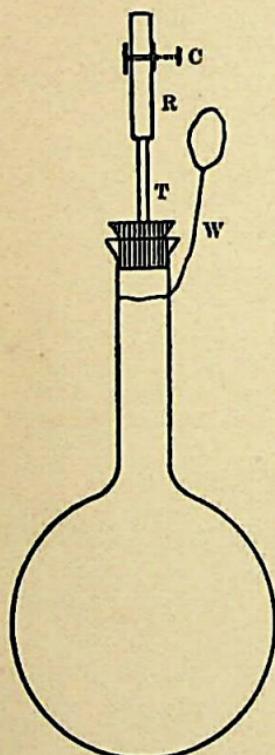
We know that $(y - x)$ cu. cm. of air weigh $(b - a)$ grm. (Experiment 26 (i).) From this we can calculate the weight of 1000 cu. cm. of air.

Example.— In an experiment the following values were obtained:—

Weight of flask + water	$= 145 \cdot 47$ grm.	(a).
,, ,, ,, ,, + air	$= 146 \cdot 17$,,	(b).
,, ,, air	$= \quad \cdot 70$,,	$(b - a)$.
Volume of water left in the flask	$= \quad 42$ cu. cm.	(x).
,, ,, ,, required to fill the flask	$= 625$,,	(y).
,, ,, air weighed	$= 583$,,	$(y - x)$.

$\therefore$ 583 cu. cm. of air weighs $\cdot 70$ grm.

$$1 \quad \text{,,} \quad \text{,,} \quad \text{weighs} \ \frac{\cdot 70}{583} \ \text{,,}$$

$$1000 \quad \text{,,} \quad \text{,,} \quad \text{weighs} \ \frac{700}{583} \ \text{,,}$$

$$= 1 \cdot 2 \ \text{,,} \quad \text{(approximately)}.$$

What effect has the presence of air upon a metal?

The effect is obtained much more quickly if the metal is heated.

Experiment 27.—(i) Take some pieces of lead-foil and scrape them with a knife. Notice the appearance of the metal before and after scraping.

Half fill a crucible with the crumpled lead-foil. Place the crucible on one pan of the balance and add lead shot or lead-foil to the other pan until the two weights are equal. The crucible is then said to be counterpoised. Leave the counter-poise on the balance pan.

Place the crucible on a pipe-clay triangle standing on a tripod (fig. 23). Heat the crucible, gently at first, and then strongly, for ten minutes. During this time write down all the changes in appearance which the metal undergoes.

Allow the crucible and its contents to cool. Replace the crucible on the pan of the balance to find whether it is heavier or lighter than its counterpoise.

(Has the metal increased or decreased in weight?)

(ii) **Is this effect peculiar to lead or common to other metals?**

Repeat Experiment 27 (i) with other metals, such as tin, iron, magnesium, and copper.

They should be in the form of foil or wire, so as to expose as large a surface as possible to the air.

In the case of magnesium very great care must be taken to prevent the loss of the white fumes which will be given off by the burning metal.

Enter your results as follows:—

Metal.	Appearance.		Increase or Decrease in Weight.
	Before Scraping.	After Scraping.	
Lead ...			
Tin ...			

The question arises, whence comes this increase in weight and change in appearance detected in Experiment 27.

Not from the crucible. Possibly from the air, since we have shown that air has weight, and the only two substances in contact with the metals are the crucible and the atmosphere. If the change in appearance of the lead in Experiment 27 *is* due to the action of the air on the metal, on excluding the air we should not get this change in appearance on heating the lead.

Let us try to exclude the air whilst heating the metal. To do so we may immerse the metal in a liquid which has no effect on the lead. A suitable liquid is melted paraffin-wax.

Experiment 28.—To see whether lead changes in appearance when heated in the absence of air.

Melt some paraffin-wax in an evaporating-dish placed on a wire gauze on a tripod.

Drop some small, bright pieces of lead-foil into the melted wax so that they are completely covered. Heat the evaporating-dish as in Experiment 27 (i).

Do you notice the same change in the appearance of the metal as was noticed in Experiment 27?

Unfortunately we cannot find whether the weight has altered, since some of the paraffin-wax will probably burn or escape as vapour.

Do the results of this experiment support or contradict the possibility of the increase in weight of a metal coming from the air?

So far we have confined our attention to the *metal*. We will now try to find out how the *air* is affected when certain substances are heated in it.

Experiment 29.—How are (i) the volume, (ii) the properties, of a small quantity of air affected when a substance burns in it?

Phosphorus is a suitable substance to use.

Take a trough and a bell-jar fitted with a stopper (fig. 25).

Stick a strip of gummed paper vertically on the bell-jar.

Cover the bottom of the trough with water.

Fig. 25.—Phosphorus burning under a Bell-jar

Stand the bell-jar in the water and mark the level of the water on the strip of paper (*a*). Float a crucible lid on the water. Place a small piece of phosphorus[1] on the crucible lid. Quickly place the bell-jar over the lid and phosphorus.

Heat one end of a glass rod in a Bunsen burner; thrust the rod through the neck of the bell-jar and touch the phosphorus. (The phosphorus will immediately catch fire.) Quickly remove the rod and insert the stopper. Notice what happens as the phosphorus burns.

[A less simple but more accurate bell-jar, B, is shown in fig. 26. T is a short glass tube into which a rubber stopper is fitted. This stopper carries a copper wire for the purpose

[1] Care must be exercised in using phosphorus, as the warmth of the hand or of the room is sufficient to ignite it. It is therefore kept under water in bottles, and when cut into pieces it is cut under water. It should be lifted from the water on the point of a knife, not by the fingers.

of igniting the phosphorus which is contained in the crucible c.
The crucible is supported on a wire ring suspended by wires
from the large rubber stopper which closes the bell-jar.   The
bell-jar is placed in a trough of water and the experiment
conducted as just described.   To ignite the phosphorus the
wire is withdrawn by means of the small stopper.   The end
of the wire is heated, and the wire and stopper tightly replaced.
The hot end of the wire touches the phosphorus and ignites
it.]
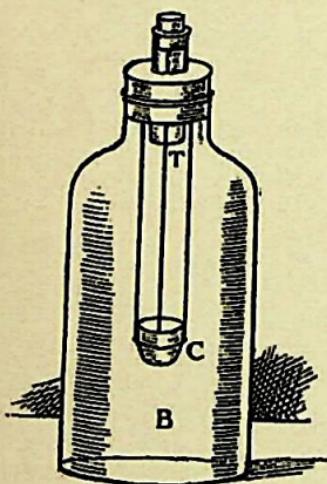
Fig. 26. — Removal of Oxygen
from a small quantity of Air by
the burning of Phosphorus in it

When all is cold again pour
water into the trough until the
water-level is the same inside the
jar as it is outside.[1]   Mark this
level (b) on the strip of paper on
the bell jar.

Light a taper, remove the cork,
and plunge the burning taper into
the bell-jar.   (What happens to the
taper?   Will the gas support com-
bustion?)

Remove the jar from the trough,
invert it, and replace the cork.
Fill the jar up to the mark (b)
with water from a measuring cylin-
der.   Note the volume.   (Volume
= x cu. cm.)   What volume of gas was left after the phos-
phorus had been burned?

Fill the jar up to the mark (a) with water.   (Volume
= y cu. cm.)   What volume of air was experimented
upon?

Calculate the percentage volume of the air used up when
phosphorus burns in air, as in the example below.

---

[1] The reason for this will be understood after reading Chapter VII.   It will
perhaps suffice for the present to remark that if the level of the water outside the
bell-jar was lower than the level of the water inside the bell-jar, the gas in the bell-
jar would be under slightly less pressure than the air with which we commenced
was under.   This difference of pressure would cause the remaining gas to occupy a
slightly larger volume than it would otherwise occupy.

Example—

Volume of water required to fill
the jar to (*a*)   = 510 cu. cm. (*y*).
Volume of water required to fill
the jar to (*b*)   = 400 cu. cm. (*x*).
Volume of air experimented upon = 510 cu. cm. (*y*).
Volume of gas removed by burn-
ing phosphorus   = 110 cu. cm. (*y* − *x*).

Percentage volume of air removed $= \dfrac{110 \times 100}{510}$

$= 21\cdot5$.

Experiment 30.—To find the effect on a small quantity of air when iron rusts in it.

For this experiment we could use the same apparatus as in
Experiment 29, but that sketched in
fig. 27 is more accurate.

Take about half a metre of glass
tube 1 cm. in diameter. Close one
end by means of a well-fitting stopper,
or preferably close it in the Bunsen
burner.

Rinse the tube out with water, and
into the damp tube put 1 cu. cm. of
bright iron filings. Shake the filings
up in the tube and they will adhere
to the wet sides. Stand the tube
mouth downward in a jar of water
(fig. 27) until the next week.

Then level the water inside and
outside the tube. Measure the length
of the column of gas left inside the
tube. Also measure the full length
of the tube. These lengths may be

Fig. 27.—Removal of Oxygen
from a small quantity of Air by
the rusting of Iron in it

taken as representing the volumes of air unused and air experi-
mented upon.

In fig. 27 the tube appears to be not quite full of air. This
is because the pressure due to the greater height of the water

in the jar than in the tube has compressed the air in the tube.
Calculate as before the percentage decrease in volume of the
air which occurs when iron rusts in it. Test the gas which
remains in the tube as in Experiment 29. Are the results of
this experiment evidence for or against
the suggestion that rusting and burn-
ing produce similar effects on the air?

**Experiment 31.—To find the
effect upon a small quantity of
air when phosphorus fumes
(burns very slowly) in it.**

Use the apparatus shown in fig. 28.

T is a glass tube 50 cm. long and
4 cm. diameter. S is a rubber stopper
from which is suspended a small
crucible. A stick of phosphorus about
1 cm. long is placed in the crucible.
The tube is then placed in a cylinder
partly full of water.

Leave the apparatus standing for a
week, or until the water ceases to rise
in the tube, then determine the per-
centage decrease in volume and change
in properties of the air as before.

Fig. 28.—Removal of Oxy-
gen from the Air by the slow
Combustion of Phosphorus

The following conclusions have been
drawn from experiments similar to
those which you have just performed.

Air consists mainly of two gases—

(a) *A gas called* **oxygen**, *which will
allow some materials to burn in it.*

(b) *A gas called* **nitrogen**, *which will not allow substances to
burn in it.*

*About 21 per cent (by volume) of the air is oxygen. The rusting
and burning of substances in the air affect the air similarly. They
remove the oxygen from the air.*

The increase in weight that occurs in certain substances

when heated in air is due to the oxygen which has been taken from the air. When a substance has been heated in air the substance is often completely changed. In fact, a new substance is formed in every case which has been considered in this chapter. The substances thus formed are called *oxides*. For example:—

Lead	on being heated in air forms			*lead oxide.*
Magnesium	,,	,,	,,	*magnesium oxide.*
Phosphorus	,,	,,	,,	*phosphoric oxide.*
Iron	on rusting		,,	*iron oxide.*

Now if we could get back from the oxide the oxygen which the substance has taken from the air it would be a conclusive proof that the increase in weight experienced by substances when heated in the air is due to the oxygen of the air having combined with them. Let us try to do so.

Experiment 32.—To find the effect of heat upon mercuric oxide.

Place a little red oxide of mercury in a hard-glass test-tube. Heat it in a Bunsen burner, gently at first and then more strongly. Light a splinter of wood, blow out the flame, and thrust the glowing end of the

Fig. 29.—Mercuric Oxide decomposed into Mercury and Oxygen by Heat

splinter well into the tube (fig. 29). Continue the heating for a few minutes, keeping the glowing splint in the tube. (What happens to the glowing splint?)

Carefully notice the substance which collects on the walls and bottom of the test-tube. Rub the substance that collects on the walls of the test-tube with a piece of glass rod. (What happens?) What effect has heat upon mercuric oxide?

History.—Oxygen was discovered by Joseph Priestley in 1774. The discovery came about in this way. Priestley was observing the effect of heat upon various substances. For convenience he enclosed the substances in a cylinder containing mercury inverted in a trough of mercury. He heated the substances by means of the sun's rays, which he focused on the substance with the aid of a burning-glass.

Priestley announced his discovery in the following words: "I endeavoured to extract air (gas) from 'mercuric oxide'; and I presently found that by means of this lens, air (gas) was expelled from it very readily. Having got about three or four times as much as the bulk of my materials, I admitted water to it, and found that it was not imbibed by it. But what surprised me more than I can well express was that a candle burned in this air (gas) with a remarkably brilliant flame."

It is claimed that Karl William Scheele had obtained the gas before Priestley's discovery, but he neglected to publish any account of his discovery until 1777. Scheele obtained the gas by heating various substances, such as mercuric oxide, saltpetre (potassium nitrate), and manganese dioxide, with sulphuric acid.

Lavoisier's proof that the increase in weight of some metals when calcined (heated) in air is due to the absorption of oxygen from the air.

Priestley informed the famous French chemist Lavoisier of his discovery. Lavoisier saw the importance of Priestley's discovery towards finding the solution of the problem: "What happens when substances are burned?" Accordingly Lavoisier heated mercury in a glass retort (T, fig. 30) connected by a bent neck with a bell-jar P, containing a known volume of air. The bell-jar stood in mercury in the trough R S. Lavoisier heated the mercury in the retort for several days, not quite to its boiling-point. During this time red specks (mercuric oxide) appeared on the surface of the mercury in T, and the mercury-level in P gradually rose. After twelve days the mercury ceased to rise, and the heating was stopped. The

volume of air in P had then decreased in volume by about one-fifth. The mercuric oxide was collected and placed in a retort. It was then heated. Oxygen was given off, and mercury was left in the retort. The volume of oxygen given off was measured. It was found to be *equal to the decrease in volume of the air in* P (fig. 30).

It will be noticed that it was not until a metal (mercury) was found which combines with oxygen at one temperature,
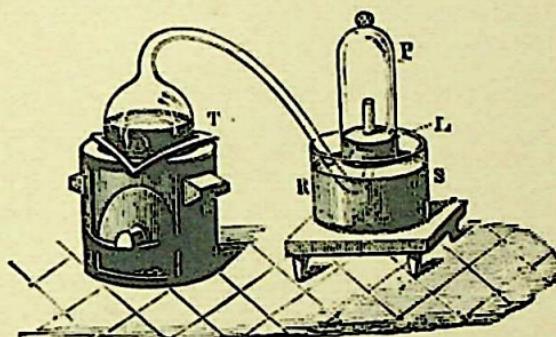
Fig. 30.—Formation of Mercuric Oxide

R, S, Dish containing mercury. P, Bell-jar. L, Level of mercury within bell-jar.
T, Glass retort containing mercury.

and parts with its oxygen at a higher temperature, that the explanation of combustion was forthcoming.

Some calcined metals (oxides) do *not* part with their oxygen on heating. We shall investigate this point in the next experiment.

Experiment 33.—To find whether oxides of metals yield oxygen on heating.

Proceed as in Experiment 32, testing in turn (*a*) red lead (an oxide of lead); (*b*) lead peroxide (another oxide of lead); (*c*) copper oxide; (*d*) iron oxide; (*e*) manganese dioxide; (*f*) barium peroxide. Classify the oxides tested according as they do or do not yield oxygen on heating.

QUESTIONS ON CHAPTER IV

1. Describe in detail the method you would use to obtain (*a*) mercuric oxide from mercury, (*b*) mercury from mercuric oxide.

2. Describe the physical and chemical changes which take place when the following substances are heated separately in air: (*a*) mercuric oxide, (*b*) copper, (*c*) manganese dioxide.

3. State exactly what happens (*a*) to the copper, (*b*) to the air, when air is passed over heated copper.

4. How do you account for the fact that when a metal is heated in air, the substance formed weighs more than the metal?

5. How do you account for the changes in colour which metals undergo when heated in air?

6. How could you obtain from the air (i) a sample of oxygen, (ii) a sample of nitrogen?

7. How would you proceed in order to prepare specimens of iron oxide and phosphorus oxide?

CHAPTER V

OXYGEN

We will now proceed to prepare and examine oxygen, but, before doing so, note that in seeking the properties of a gas, experiments should be performed upon it in order to enable you to answer the following questions.   [These questions are reprinted in the Appendix to facilitate reference to them.]

(i) What is the colour of the gas?

(ii) Has the gas any distinctive smell?[1]   (If so, try to remember the smell.)

(iii) Will the gas burn?   That is, when you thrust a lighted

---

[1] In smelling a gas do not inhale (breathe in) a large quantity of the gas, as some gases are very poisonous.   When the preparation of such a gas is described in this book, a note to keep .... nature will be added.

taper into a jar of the gas, does the gas burn at the mouth of the jar (fig. 31).

(iv) Will the gas support combustion? That is, when you thrust a lighted taper into a jar of the gas, does the taper continue to burn?

(v) Is the gas insoluble, slightly soluble, or very soluble in water?

(vi) Does the gas give an acid or an alkaline or a neutral solution?

A piece of purple litmus-paper should be placed in the solution of the gas in water to see whether it turns the litmus red or blue. Solutions which turn the litmus-paper red are said to be acid solutions. Those which turn the litmus-paper blue are called alkaline solutions.

(vii) What other properties has the gas?

To enable you to answer this question, special experiments will be described for each gas when it is studied.

Fig. 31.—Taper extinguished but gas burning

Methods of preparing Oxygen.

As we have seen in Experiments 32 and 33 oxygen may be prepared by heating *mercuric oxide, barium peroxide, manganese dioxide, red lead,* and *lead peroxide.* It has also been stated (p. 44) that *saltpetre* on heating yields the gas.

Potassium chlorate is another substance which gives off oxygen when heated, and since it is fairly cheap, this substance is generally used in the laboratory when we wish to prepare oxygen.

It has also been found that the potassium chlorate need not be heated so long if it is mixed with about one-quarter of its weight of manganese dioxide.

Experiment 34.—To prepare oxygen and examine its properties.

(i) Take about 15 grm. of potassium chlorate crystals. Add

to them about 4 grm. of manganese dioxide, and mix the two substances well together on a sheet of paper.

Place the mixture loosely in the flask A, fig. 32. Fit the flask with a well-fitting cork having a single hole. Select a glass delivery tube B, and fit it through the cork. Support the flask on a retort-stand using two rings and a wire gauze.

Take a pneumatic trough C, and a bee-hive shelf F. Partly fill the trough with water until the water is about half an inch above the bee-hive shelf. Fill a gas-jar D, with water. Place a greased[1] ground-glass plate over the mouth of the gas-jar. Invert the gas-jar, and place it on the bee-hive shelf. Slide off the
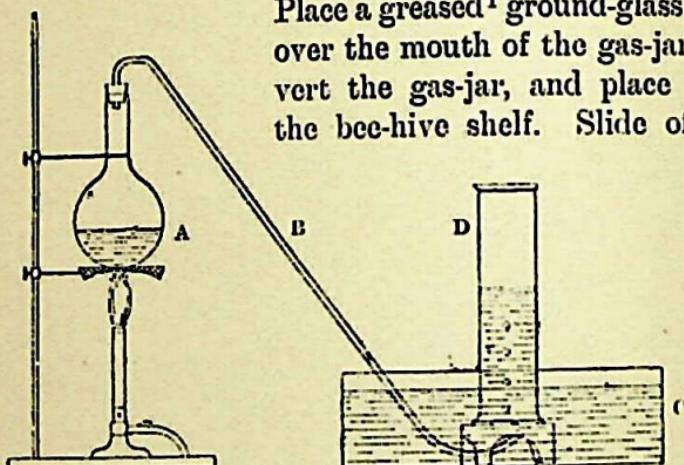
Fig. 32.—Preparation of Oxygen from Potassium Chlorate

glass plate and the gas-jar is ready for collecting the gas by the displacement of water.

Place the end of the delivery-tube under the bee-hive shelf, and commence heating the oxygen mixture, gently at first and afterwards more strongly.

Bubbles of oxygen will rise through the water in the jar. Observe carefully any change in size of the bubbles, for their behaviour will give you some indication as to the solubility of the gas. [This does not hold good in the case of the first jar of gas collected, for *it* will partly consist of the air contained in A at the commencement of the experiment.]

Continue heating until the jar is full of oxygen. Then lift the gas-jar slightly, slide under it the glass plate (greased side

upward), and lift the gas-jar from the trough. Place it on the bench with the glass plate uppermost.

Collect in this way two gas-jars and a test-tube full of oxygen. Then remove the delivery-tube from the trough, and stop the heating. [Be careful not to take away the Bunsen burner before the removal of the delivery-tube.]

Examine the gas according to the scheme given on p. 46 or in Appendix I.

(ii) Questions (i) and (ii), p. 46, can be answered without interfering with the jars of oxygen collected.

Questions (v) and (vi) can be answered by placing the test-tube of the gas, mouth downwards, in a beaker containing a little water. If the gas is soluble in water the water will rise in the test-tube. Test the water in the tube with litmus.

Questions (iii), (iv), and (vii) may be conveniently answered by each member of the class using his second jar of gas to perform one of the following tests.

Fig. 33.—
Deflagrat-
ing-spoon

Experiment 35.—Combustion in oxygen.

Fig. 34.—Combustion in Oxygen

(i) Light a splinter of wood. Remove the glass plate from your jar of oxygen, and quickly insert the splinter. (What happens?) Withdraw the wood, blow out the flame, and insert the glowing end well into the jar. (What happens?) Does the gas burn, or the wood, or both? Answer Questions (iii) and (iv), p. 47.

(ii) In a deflagrating-spoon (fig. 33) place a small piece of carbon (charcoal). Heat the deflagrating-spoon and carbon in a Bunsen burner until the carbon glows. Remove the glass plate from the jar of oxygen, and place the deflagrating-spoon in the jar (fig. 34). (What happens?) Remove the deflagrating-

5
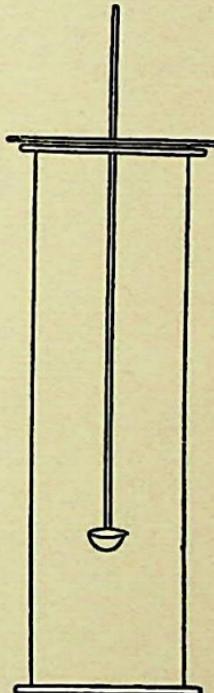
spoon, then cover the jar with the plate, and label this jar *carbon dioxide.* Make a second jar of carbon dioxide in a similar manner.

(iii) Proceed as in (ii), using sulphur instead of carbon, and heating it in the Bunsen burner until it burns.   Label the jar of gas produced by the combustion of the sulphur in oxygen, *sulphur dioxide.*

(iv) Proceed as in (ii), using a very small piece of *phosphorus.* Instead of heating the deflagrating-spoon to ignite the phosphorus merely touch the phosphorus when on the spoon with the hot end of a glass rod.

Label this jar *phosphorus pentoxide.*

Fig. 35.—Iron burning in Oxygen

(v) Proceed as in (ii), using a very small piece of *sodium.*

Sodium is to be kept away from water— even from moist fingers.   When you lift it, do so with the point of a penknife.

The sodium should be placed in the deflagrating-spoon and heated until it begins to burn.

Label this jar *sodium oxide.*

(vi) Proceed as in (ii), using 10 cm. of *magnesium* wire.   One end of the magnesium wire should be twisted round the deflagrating-spoon, and the other end lighted in the Bunsen burner.   The deflagrating-spoon should then be plunged into the gas jar of oxygen.

Label this jar *magnesium oxide.*

(vii) Proceed as in (ii), using a spiral of very thin *iron wire.* The wire used by florists is suitable.   Pour into the jar of oxygen sufficient water to cover the bottom of the jar.   This will prevent falling pieces of hot iron oxide from cracking the jar during the experiment.   Make the wire into a coil, and then make one end of the coil white-hot in the Bunsen burner. Dip the hot end into some sulphur, and then while the sulphur is burning quickly plunge the wire into the jar of oxygen (fig. 35).   If the iron fails to burn, it is probably because it was not hot enough.   Try again.

Label this jar *iron oxide.*

Experiment 36.—To examine the oxides produced.

First take the jar containing the iron oxide. Examine a piece of the solid oxide. [It is called *magnetic oxide* of *iron* to distinguish it from the reddish-brown oxide of iron (rust), which is called *ferric oxide*.] Find whether it is soluble in water or not. See whether it affects purple litmus-paper or not. Next, shake up the contents of the other jars with a *little* water, and add purple litmus-paper or solution to the contents. Are the remaining oxides soluble or insoluble in water? (Only soluble substances can affect litmus.) Which of them give acid and which give alkaline solutions? Rub your fingers together in the solution of sodium oxide, and notice the soapy feeling and detergent (cleansing) properties of the solution.

Take another jar of carbon dioxide and shake up the contents with clear lime-water. Observe that carbon dioxide turns the lime-water milky. There is only one other gas we shall study—sulphur dioxide—which has this property, and since the latter gas is easily distinguished by its smell, this test will in future experiments enable us to identify carbon dioxide. Draw up a table of results as follows:—

Oxide.	Description of the Oxide.	Is the Oxide Soluble or Insoluble in Water?	Is the Solution of the Oxide Acid or Alkaline?	What effect has the Oxide on Lime-water?
Carbon dioxide	Colourless gas.	Soluble.	Acid.	Lime-water turns milky.
Sulphur dioxide				

The oxides of carbon, sulphur, and phosphorus dissolve in water and form acid solutions. They are therefore called *acid oxides*. Their solutions in water are called *acids*. [All acids are not solutions of acid oxides in water, e.g. hydrochloric acid is not, but all solutions in water of acid oxides are acids.] *Acid oxides* are sometimes called *anhydrides*. The word anhy-

dride means "without water"; *with* water an anhydride becomes an acid.

Substances (like carbon, phosphorus, and sulphur) which unite with oxygen to give acid oxides are called *non-metals*.

The oxides of sodium and magnesium dissolve in water and form alkaline solutions. They are called *basic oxides*. Their solutions in water are called *hydroxides*.

Most basic oxides (like iron, tin, and copper) are insoluble in water, and so do not form hydroxides on the addition of water. Hydroxides of these metals can be formed by other methods, and they and the oxides behave towards acids similarly to the soluble basic oxides (see Chapter IX). Hence these also are called basic oxides.

Substances (like sodium, magnesium, iron, tin, and copper) which unite with oxygen to give basic oxides are called *metals*.

a metal   *a non-metal*

combined with oxygen forms

a basic oxide   *an acid oxide*

which combined with water forms

a hydroxide   *an acid*

which combine and form

a salt
+ *water* (see Chapter IX).
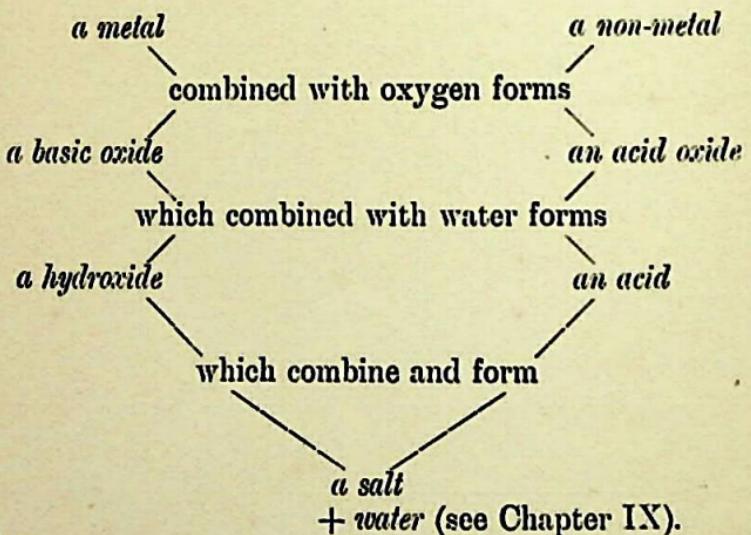
Thus—

carbon dioxide combines with water and forms			*carbonic acid.*
sulphur dioxide	,,	,,	,,	*sulphurous acid.*
phosphorus pentoxide	,,	,,	,,	*phosphoric acid.*
sodium oxide	,,	,,	,,	*sodium hydroxide* (caustic soda).
magnesium oxide	,,	,,	,,	*magnesium hydroxide.*

Properties of Oxygen.—Oxygen is a colourless, tasteless, and odourless gas. It is slightly heavier than air.

Oxygen is slightly soluble in water.[1] A hundred volumes of water will dissolve four volumes of oxygen at 0° C.

The gas is necessary for the support of life, and is used by doctors in cases where, owing to illness, an insufficient supply of oxygen is inhaled.

Oxygen itself will not burn, but supports combustion vigorously. For example, it will rekindle a glowing splint. All substances that will burn in air, burn in oxygen with very much greater brilliance.

The products formed when substances are burnt in oxygen are called oxides. The different kinds of oxides formed and their action upon water has already been given (p. 51).

QUESTIONS ON CHAPTER V

1. Describe the chemical changes which take place when (a) sodium, (b) iron, (c) sulphur are burned in oxygen.

2. Name all the substances you know which yield oxygen on heating.

3. Name the two classes of oxides studied, and state the chief properties of the members of each class.

4. What is an anhydride? Name three anhydrides, and state of what substance each is the anhydride.

5. What is a hydroxide? How could you prepare a solution of sodium hydroxide?

6. How would you prepare and collect oxygen gas? Sketch the apparatus you would use.

7. You are given three gas-jars, each containing oxygen. Describe in detail how you would proceed in order to convert the oxygen in them into iron oxide, magnesium oxide, and sulphur dioxide respectively.

8. Describe the preparation and properties of oxygen.

[1] See Table of Solubilities of Gases (p. 316).

CHAPTER VI

PRELIMINARY CHEMICAL STUDY OF WATER.
HYDROGEN

[*Throughout this chapter care must be taken to avoid explosions. Note carefully the detailed instructions given.*]

In this chapter it is assumed that the student is already acquainted with the following physical properties of water.[1]

(*a*) The density of pure water. 1 cu. cm. of pure water at 4° C. weighs 1 grm., (*b*) the boiling-point of pure water under a pressure of 76 cm. of mercury is 100° C., (*c*) the freezing-point of pure water is 0° C.

These three constants of a pure substance—the density, the boiling-point, and the freezing-point—are very useful in enabling us to identify the substance; for it is very unlikely that there will be two substances having the same boiling-point, the same freezing-point, and the same density.

In our preliminary study of air, by removing the oxygen, we were able to show that air contains oxygen and nitrogen. This was accomplished by heating certain metals in air. (Chapter IV.)

Let us now find the effect some metals have upon water, for perhaps this will enable us to answer the question: Of what is water composed?

If the metals show no effect with cold water, we will try the experiment with boiling water or steam, and, if necessary, with heated metal.

Experiment 37.—To study the effect of the metal sodium upon cold water.

Take two beakers, a small one and one sufficiently large to cover the other, as in fig. 36.

Cover the bottom of the small beaker with water.

Take a piece of sodium not larger than a small pea—a large piece would be dangerous—and drop it into the water in the small beaker. Cover the small beaker with the larger one to

protect yourself from small pieces of sodium which may be shot out from the metal.

State all you observe.

When the action ceases, place a piece of neutral litmus-paper in the water in the small beaker. Is the liquid alkaline or acid? Also rub your fingers together in the liquid. Of what solution already studied does the feel of the liquid remind you?

Experiment 38.—To collect and examine the gas given off when sodium acts upon water.

Fig. 36.—Effect of Sodium upon Water

Take a pneumatic trough and pour a little water into it. Fill a gas-jar with water, and invert the jar in the trough. *There must be no air in the gas-jar or an explosion may occur* when testing the gas. Cut off about 1 cu. cm. of sodium and wrap it in lead-foil. Make a few holes in the foil about as large as a pin head, so that the water can come in contact with the sodium. *It is dangerous to make a large hole, from which the sodium or pieces of it could escape* and float to the top of the water during the experiment. Drop the sodium in its covering into the trough and cover it with the gas-jar full of water (fig. 37). Wait till bubbles of gas cease to rise from the sodium. When the action ceases, slide the greased

Fig. 37.—Preparation of Hydrogen from Water by means of Sodium

plate under the gas-jar, and remove the jar of gas from the trough. Stand it on the bench with the greased plate downward until required.

Examine the gas according to the scheme in p. 46, applying only Tests (i), (ii), (iii), (iv).

What is the most noticeable property of the gas?

The gas you have just collected is called *hydrogen*.

The question now arises: "Does the hydrogen come from the sodium or from the water?"

It will perhaps help us to answer this question if we try other metals. Experiment 37 may be repeated, using potassium or calcium, and hydrogen will be obtained. With other metals and cold water there is no effect. We will next try steam and heated magnesium and then steam and heated iron.

Experiment 39.—(i) **To find whether hydrogen is given off when steam is passed over heated magnesium.**
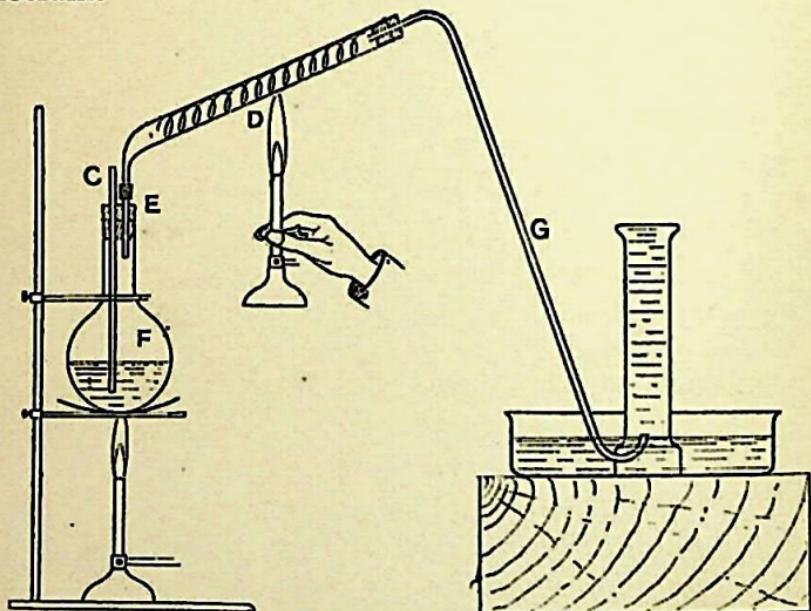
Fig. 38.—Preparation of Hydrogen from Steam by means of Heated Magnesium

Fit up the apparatus shown in fig. 38.

F is a 250-cu.-cm. flask half full of water.

C is a straight piece of glass tubing to act as a safety-valve. If the pressure in F gets too great during the experiment the water vapour may blow out through C instead of causing an explosion. Note the position of the bottom of the tube C. D is a combustion tube from which the tip has been cut off,

and which is connected by rubber tubing to the piece of glass tubing E.

D should be arranged to slope down towards the flask so as to prevent the condensed steam from coming in contact with the hot part of D and cracking the tube. Take about 30 cm. of magnesium wire. Wind it round a piece of glass tubing, to make it into a spiral, and slide the coil of wire into D.

Insert the stopper carrying the delivery-tube G into the wide end of D. Set up the pneumatic trough, &c., as in the figure, but do *not* yet place the gas-jar on the beehive shelf.

Boil the water in F, and when steam has been coming off freely for a few minutes all the air will have been swept out of the apparatus by the steam.[1] *Now* place the gas-jar on the beehive shelf.

While the steam is passing over it heat the magnesium in D by means of the Bunsen burner.

When the magnesium begins to burn in the steam, gas will collect in the gas-jar. Then remove the delivery-tube from the trough and extinguish the flame of the burner under the flask.

Describe what happened to the heated magnesium as the steam passed over it.

Test the gas as in the last experiment. Has it the same properties as the hydrogen obtained by the action of sodium upon water?

(ii) Examine the substance left in the tube D. Does it look like magnesium oxide? Refer to p. 51, and examine this substance as there directed. Is the substance somewhat soluble in water, as magnesium oxide is? Does it give an alkaline solution, as magnesium oxide does?

(iii) Experiment 39 (i) may be repeated, using iron filings instead of magnesium, and an iron tube may if desired be used in place of the glass tube D. If an iron tube is used it may with advantage be placed horizontally to prevent the filings slipping into the flask or plugging up the steam tube.

[1] Without this precaution a mixture of air and hydrogen will be collected, which will explode on testing with a lighted taper.

We have now seen that *sodium, potassium*, and *calcium*, when placed on cold water, set free the gas hydrogen, and that magnesium and iron set free hydrogen if heated in steam. Other metals which will act in a similar manner but at varying temperatures are zinc, manganese, cobalt, barium, and strontium.

It appears, then, either (i) that all these metals contain hydrogen, or (ii) that water contains hydrogen.

Now on examining the substance left when magnesium is used, as far as we can tell it is identical with the magnesium oxide formed when magnesium burns in oxygen. This seems to indicate that the hydrogen has come from the water, and it also supports the probability that the water not only contains hydrogen but also oxygen.

Let us consider again the products of the action of sodium on water. If the sodium behaved in a similar manner to the magnesium it should have become sodium oxide when it set free the hydrogen from the water.

Now sodium oxide is soluble in water, and gives a basic solution which feels soapy to the touch (see p. 51).

Had the liquid which was left after sodium acted upon water these two properties?

Although these results do not prove conclusively that water contains hydrogen and oxygen, they indicate the strong probability that it does.

It will help us to a correct knowledge of the composition of water if we burn hydrogen in air and collect the substance formed.

It is not *convenient* to make hydrogen by the action of a metal on water. A much more convenient way is by the method given in Experiment 40, and if hydrogen is used this method of generating it should be adopted.

Coal-gas contains about half its volume of hydrogen, and since the other gases present do not adversely affect the experiment, coal-gas might be used instead of hydrogen in the following experiment, but the experiment would then, strictly speaking, no longer be a proof of the composition of water.

Experiment 40.—(i) To prepare hydrogen by the action of zinc on sulphuric acid.

Fit up the apparatus shown in the diagram (fig. 39). The thistle funnel T must touch the bottom of the bottle or flask W. Remove the stopper and place in the flask about 10 grm. of granulated zinc. Pour dilute sulphuric acid down the thistle funnel until the acid covers the zinc. A rapid stream of hydrogen will be given off from the acid. The gas coming out of the delivery-tube will be hydrogen mixed with the air which was in the flask. This, as you know, is an explosive mixture. Collect a test-tube full of
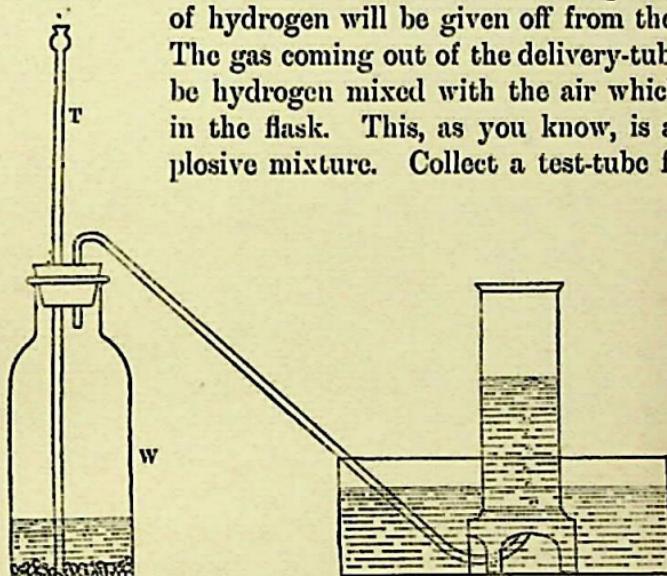
Fig. 39.—Preparation of Hydrogen from Sulphuric Acid by means of Zinc

the gas by displacement of water, as in Experiment 34. Close the open end of the test-tube with the thumb, and carry the test-tube to a flame at least a metre distant from your apparatus. Remove your thumb, and put the open end of the test-tube to the flame. A slight explosion will probably occur. Collect several tubes full of the gas and test them in the same way. You will, after a time, get a specimen of gas which does not explode when you test it at the flame, but which burns with a blue flame. Then you know that the dangerous mixture has been removed from the flask, and that hydrogen *only* is coming off.

If the evolution of hydrogen ceases, or becomes too slow,

more acid must be poured down the thistle funnel. Collect two or three gas-jars or test-tubes full of hydrogen by displacement of water, and then remove the delivery-tube from the trough.

(ii) *To determine the properties of hydrogen.*

Examine the gas collected by the scheme given in p. 46.

Try to pour the hydrogen from a gas-jar upward into a vessel containing air (fig. 40). Close both vessels with greased plates, and test the contents of each with a flame. Did you succeed in pouring your hydrogen upward? Is hydrogen lighter than air?

Make a list of the properties of hydrogen from the results of your experiments.

Properties.—Hydrogen is a colourless, invisible, tasteless, and odourless gas. It is the lightest substance known. (A litre of hydrogen weighs ·09 grm.) For this reason, when we are comparing the densities of gases, we count hydrogen as having a density of 1.

Fig. 40.—Hydrogen being poured upward from A into B

Hydrogen will not support combustion, but burns in air or oxygen with a very hot, non-luminous flame. When mixed with air it explodes if a flame be applied. It is very slightly soluble in water, and the solution is neutral to litmus-paper (see Appendix II).

Distribution.—Free hydrogen is found on the earth only in very small quantities. It occurs in volcanic gases. Enormous quantities of incandescent hydrogen surround the sun, and the gas is also present in some stars. As a constituent of other substances hydrogen is very abundant.

History.—The production of hydrogen from iron and sulphuric acid was known previous to the year 1600.

J. B. van Helmont (1609), in his description of the gas, mentions the facts that it will burn but will not support combustion. For this reason it was then called "inflammable air".

There are other gases which will burn. Those of them which were then known were also called "inflammable air". Thus several distinct gases were confused, and looked upon as one gas, because they all would burn.

In 1766 Cavendish showed that the gas obtained when iron is dissolved in sulphuric acid was a gas distinct from the other "inflammable gases".

About seventeen years later this gas was named hydrogen. (See p. 74.)

Experiment 41.—(i) To collect the substance formed when hydrogen burns in air.
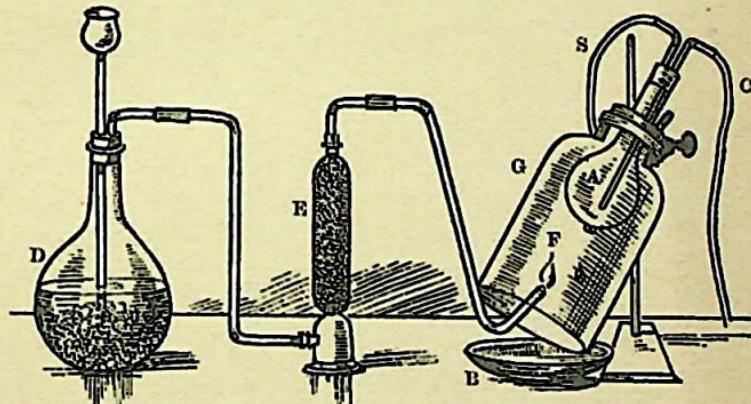
Fig. 41.—Production of Water by the Combustion of Hydrogen in Air

Set up the apparatus as shown in fig. 41.

A is a flask into which cold water flows by means of the tube C, and overflows to the sink at S. The outside of A must be perfectly dry.

The neck of A is fixed through a stopper in the bell-jar G.

C is connected either to the water-tap or a large elevated bottle of water.

B is a small dish to collect the substance formed.

D is an apparatus similar to that used for generating hydrogen in Experiment 40.

E is a tower containing granular calcium chloride to dry the hydrogen.

Pour some sulphuric acid down the thistle funnel of D, and test the gas issuing from F as in Experiment 40. When you are absolutely certain that the gas is hydrogen unmixed with air,[1] light the gas at the end of the tube.

Direct the burning hydrogen against the bottom of the flask A, and keep a stream of cold water flowing through the flask.

Observe the outside surface of the flask, and adjust the dish B so as to collect the liquid which drips from the bottom of the flask A. Collect as much of the liquid as time will permit.

(ii) To identify the liquid produced when hydrogen burns in air.

The liquid collected by each student will be so small that it is advisable to pour it all into one vessel, and to make a class examination of it.

(a) To find the density of the liquid.

Into a weighed crucible place 5 cu. cm. of the liquid by means of a pipette. Weigh it and calculate the weight of 1 cu. cm. of the liquid.

(b) To find the boiling-point of the liquid.

Pour 2 or 3 cu. cm. of the liquid into a test-tube fitted with a two-hole cork. Fix a thermometer through one hole of the cork so that the bulb is just above the liquid. The other hole, which might have a piece of glass tubing through it, serves as an outlet for the vapour.

Gently boil the liquid in the tube by means of a small flame, and take the temperature.

(c) To find the freezing-point of the liquid.

If ice is available, place the test-tube used in (b) and its

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[1] If there is any air mixed with the hydrogen, on applying a light to F the contents of the apparatus will explode.

contents in a freezing-mixture composed of ice and salt. Loosen the stopper and stir the liquid in the test-tube with the thermometer or a piece of wire, and take the temperature immediately the liquid begins to solidify.

Compare the boiling-point, freezing-point, and density of the liquid with the corresponding values for water.

Note the smell and colour of the liquid, and find its action on litmus-paper. What is the liquid?

The experiment just performed proves that when hydrogen burns in air, water is produced; but—

(i) it does not prove that the nitrogen of the air takes no part in the reaction;

(ii) it does not prove that *only* water is formed.

We shall later have to determine in what proportions by volume hydrogen and oxygen unite to form water (p. 64). We will then repeat the famous experiment of Cavendish, who burned hydrogen in oxygen, and collected *all* the products of the reaction, and found that water and *only* water was formed.

Our proof of the qualitative composition of water is now complete. *Water consists of the two gases hydrogen and oxygen. In fact water is an oxide of hydrogen.*

QUESTIONS ON CHAPTER VI

1. What happens when a piece of metallic sodium is put into water?

2. Explain the meaning of the terms: "density", "boiling-point", and "freezing-point", and indicate their value in the identification of a substance.

3. How would you proceed in order to prepare a specimen of caustic soda from sodium?

4. What effect have the following metals upon (i) cold water, (ii) steam? Sodium, calcium, silver, magnesium, lead, and copper.

5. When steam is passed over heated iron, explain what happens (i) to the iron, (ii) to the steam.

6. Water is hydrogen oxide. How would you demonstrate the truth of this assertion?

7. How may hydrogen be prepared? State the chemical and physical properties of the gas.

CHAPTER VII

COMPOSITION OF WATER BY WEIGHT AND VOLUME

In Experiment 41 we built up water from its elements. We will repeat the experiment, but arrange it so that we can measure the volumes of hydrogen and oxygen which combine to form water. We will thus determine the composition of water by volume.

In measuring the volumes of gases for comparison we must always either (i) measure them at the same temperature and pressure or (ii) note the temperature and pressure under which their volumes are measured, and calculate what the volumes would have been if they had been measured at the same temperature and pressure.

If method (ii) is adopted the pressure selected is usually the pressure of 760 mm. of mercury, and the temperature selected is 0° C.

The volume so calculated is then said to be the volume at normal temperature and pressure.

To determine the composition of water by volume we will collect in a tube over mercury known volumes of hydrogen and oxygen, and explode them by means of an electric spark. We will measure the volume of the gas left in the tube after the explosion, and find whether it is oxygen or hydrogen. We will endeavour to measure these three volumes at the same temperature and under atmospheric pressure. We shall then be able to state the proportions by volume in which hydrogen and oxygen unite to form water.

Experiment 42.—To determine the composition of water by volume.

The apparatus used is called a eudiometer, and the one represented in fig. 42 is Hoffman's type. Open the tap s¹ and completely fill the eudiometer with clean, dry mercury. Close the tap s¹.

Open the tap s and run nearly all the mercury out of the limb A. Close the tap s.

Take the hydrogen apparatus with drying-tube as used in Experiment 41. Attach to the drying-tube a long delivery-tube which can be thrust down the limb A so that the end bends round under limb B of the eudiometer. When you are certain that dry hydrogen, unmixed with air, is coming out of the delivery-tube, thrust the delivery-tube down A, and collect about 20 cu. cm. of hydrogen in B. See fig. 44. Remove the delivery-tube and make the mercury in A level with the mercury in B by pouring mercury in at the top of A, or withdrawing it at the tap s. Read the volume of hydrogen collected. For convenience the limb B is graduated in cubic centimetres.
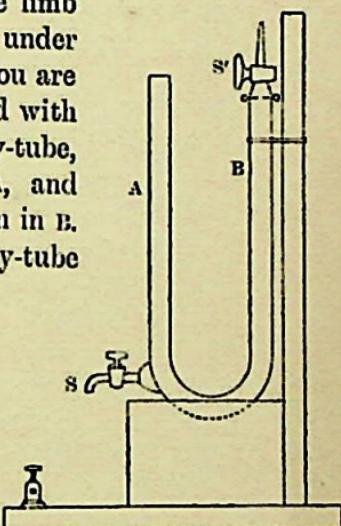
Fig. 42.—Hoffman's Eudiometer

Fit up the apparatus used in Experiment 34 for the preparation of oxygen, but use only potassium chlorate, which gives purer oxygen than is obtained from "oxygen mixture". Fit the apparatus with the drying-tube and delivery-tube just used for hydrogen, and after heating the potassium chlorate for a few minutes, to remove the air from the apparatus, collect about 10 cu. cm. of oxygen in the eudiometer. Level the mercury in A and B as before, and read the volume of oxygen collected.

The gases are now to be burned or exploded.

Securely cork up the limb A of the eudiometer to prevent the expulsion of the mercury when the gases are exploded. Connect the wires beneath s¹ to the secondary terminals of

an induction coil.[1] Join two Bunsen cells to the primary terminals of the induction coil, and switch on the current. What happens to the gases in the cudiometer? Remove the stopper from A and level the mercury in A and B as before. Read the volume of gas remaining. Almost fill A with mercury, and open the tap s^1 slightly to allow the remaining gas to escape very slowly. Test the gas with a lighted match to see whether it is hydrogen or oxygen. Enter your results as below.

Calculate the volume of hydrogen which unites with one volume of oxygen to produce water as in the example below.

Example—

Volume of hydrogen in eudiometer	=	24·2 cu. cm.
Volume of oxygen in eudiometer	=	10·4 ,,
Volume of hydrogen in A after exploding	=	3·4 ,,

∴ 10·4 cu. cm. of oxygen combine with $(24·2 - 3·4)$

= 20·8 cu. cm. of hydrogen,

i.e. 1 cu. cm. of oxygen combines with 2 cu. cm. of hydrogen.

If you repeat the experiment, using different volumes of hydrogen and oxygen, you will find in every case that each cubic centimetre of oxygen will combine with exactly 2 cubic centimetres of hydrogen, and that the water produced renders the inside of the cudiometer misty. If more oxygen is present than the hydrogen can combine with, the excess of oxygen remains after combination has taken place. If an insufficient supply of oxygen is present the excess of hydrogen will remain.

Thus, if 50 cu. cm. of hydrogen are exploded with 20 cu. cm. of oxygen, 10 cu. cm. of hydrogen will be left.

If 20 cu. cm. of hydrogen are exploded with 50 cu. cm. of oxygen, 40 cu. cm. of oxygen will be left.

This experiment was first performed by an English chemist named Cavendish. His method was similar to that employed above, but his apparatus was somewhat different. He repeated the experiment several times, and obtained sufficient liquid to test, and so showed that it was water.

There is another but less satisfactory method of showing

[1] See p. 388, *A Course of Physics*, published by Messrs. Blackie & Son.

that water is composed of two volumes of hydrogen united with one volume of oxygen. In this method we do not *build up* water from hydrogen and oxygen, but *split up* the water by means of a current of electricity into hydrogen and oxygen.

Pure water will not allow a current of electricity to flow through it, but if a few drops of concentrated sulphuric acid be added to the water the current can then flow through the water. This necessary addition of sulphuric acid constitutes a weakness of the proof. It *can* be shown, however, that the quantity of sulphuric acid present after the water has been broken up into hydrogen and oxygen is exactly the same as before. This fact renders the "proof" more satisfactory.

Experiment 43. — To electrolyse water.

To electrolyse means to split up by means of a current of electricity.

Take a voltameter as shown in fig. 43. Open the taps T_1, T_2, and fill the apparatus with water containing a few drops of concentrated sulphuric acid.

Fig. 43.—Water Voltameter

Turn off the taps. Connect the terminals S_1, S_2 to a battery of two or three Bunsen cells, and allow the current to flow for a few minutes. Now open both taps slightly to allow the gases collected to escape, and then turn off both the taps at the same instant. Proceed to collect the gases that appear in the tubes. When a reasonable quantity of the gases has been collected, switch off the current. Measure the volumes of gases collected, and test each gas by holding a lighted match at the slightly open tap. P
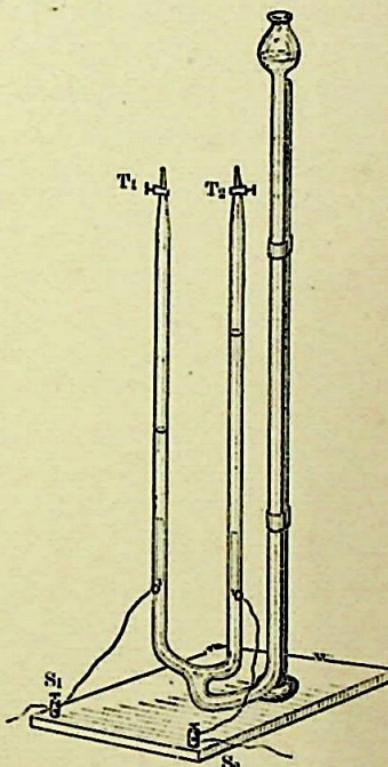
It will be seen that the volume of hydrogen collected is twice as large as the volume of oxygen. Notice that the hydrogen is set free at the *cathode* (the platinum plate which is connected to the zinc or negative pole of the battery).

For this reason hydrogen is said to be an electro-positive substance.

Oxygen is said to be electro-negative, since it is set free at the *anode* (the platinum plate which is connected to the carbon or positive pole of the battery).

Mixed Gases. — It is sometimes convenient to have the oxygen and hydrogen collected together instead of separately. In this case the apparatus shown at F (fig. 44) is useful.
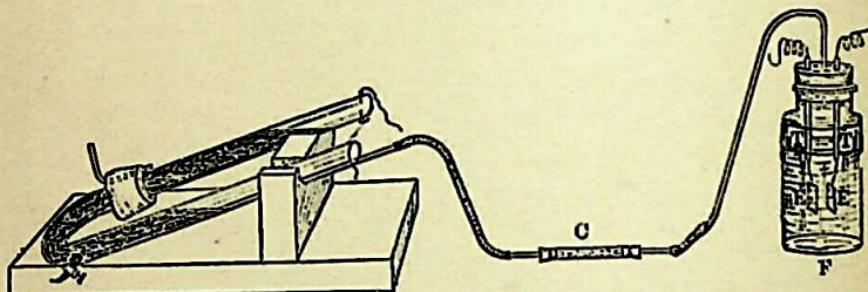
Fig. 44.—Method of filling a Eudiometer with two volumes of Hydrogen and one volume of Oxygen

It consists of a small bottle containing dilute sulphuric acid. The bottle is fitted with a three-hole rubber stopper. Two pieces of platinum-foil E, E are joined to platinum wires, which are fused into pieces of glass tubing T, T.

A little mercury is placed in T, T, and the wires from the battery are thrust into this mercury. In this way contact can be made between the electrodes (E, E) and the battery terminals.

Experiment 43 confirms the fact that two volumes of hydrogen unite with one volume of oxygen to form some water.

We will now collect the water in the form of a gas, or, more strictly, a vapour, and measure the volume of water vapour (steam) produced.

Experiment 44. — To find the volume of steam

produced when two volumes of hydrogen unite with one volume of oxygen.

Use the eudiometer employed in Experiment 42 (fig. 42). See that the tap of the eudiometer is closed. Partly fill the eudiometer with mercury as described in Experiment 42.

We must next introduce into the eudiometer a mixture of two volumes of dry hydrogen and one volume of dry oxygen. The simplest method of so do-
ing is as follows:—

Acidulated water is elec-
trolysed in an apparatus
similar to that described
on p. 68. By this arrange-
ment mixed gases in the
required proportion are ob-
tained. The delivery-tube D
is connected with a drying-
tube C containing calcium
chloride. C is connected to
a glass tube long enough
to reach round the bend of
the eudiometer. Connect
the terminals of a battery
to E, E. Allow the current
to flow for some minutes.
This will allow time for the

Fig. 45.— Apparatus for the Combination of two volumes of Hydrogen and one volume of Oxygen to form two volumes of Water Vapour

mixed gases liberated to displace the air from the bottle F. Then collect enough of the mixed gases to fill the closed limb of the eudiometer about one-third, as in fig. 44.

We have next to arrange that the water produced when the gases are exploded is in the form of steam.

To do so, surround the closed limb of the eudiometer with a larger tube called a vapour-jacket J (fig. 45). Arrange the remainder of the apparatus as shown in fig. 45. F is a flask containing amyl alcohol which boils at 130° C. The exit-tube G from the vapour-jacket should be connected to a condenser to condense the amyl alcohol vapour. Pass the vapour from

the boiling amyl alcohol through the vapour-jacket. Note the effect on the volume of mixed gases in the eudiometer. When the volume of mixed gases is constant, level the mercury in the two limbs of the eudiometer. Then read the volume of mixed gases. One-third of this volume consists of oxygen, the remaining two-thirds being hydrogen.

We must next explode the mixture.

Securely cork the open limb of the eudiometer. Explode the gases as in Experiment 42.

Remove the cork from the open limb of the eudiometer. Level the mercury in the two limbs. Read the volume of the gas (steam) now in the eudiometer.

Note that the volumes of the hydrogen, oxygen, and steam have all been measured at the same temperature (130° C.), and under the same pressure (atmospheric pressure). The volumes are therefore comparable (see p. 64).

It will be found that the volume of steam is two-thirds of the volume of mixed gases exploded.

Hence we conclude that—

$$2\begin{Bmatrix}\text{volumes of}\\\text{hydrogen}\end{Bmatrix} \text{unite with } 1\begin{Bmatrix}\text{volume of}\\\text{oxygen,}\end{Bmatrix} \text{and produce } 2\begin{Bmatrix}\text{volumes of}\\\text{steam.}\end{Bmatrix}$$

Composition of Water by Weight.—We will next determine in what proportions *by weight* hydrogen and oxygen combine to form water. To do so we will build up water from its elements, and weigh the oxygen used and the water produced, and by subtraction obtain the weight of the hydrogen which has combined with the oxygen.

We will obtain the hydrogen in the usual way, but we will obtain the oxygen that is required from copper oxide. (Hydrogen will remove the oxygen from heated copper oxide and reduce the copper oxide to copper.) The water may be collected in a tube containing either calcium chloride or concentrated sulphuric acid. To ensure that *all* the water collected comes from the union of the hydrogen and oxygen employed, we must first dry the copper oxide and its containing-tube, and also the hydrogen used.

Experiment 45.—To determine the composition of water by weight.

Select about 12 in. of combustion tubing, preferably of Jena glass. Fit it with rubber stoppers bored with one hole (C, fig. 46). Fill the combustion tube with granular copper oxide. The copper oxide will contain moisture. *We must dry the copper oxide.*

Connect one end of C to a drying-tube of calcium chloride. Connect the other end to an aspirator. Place the combustion-
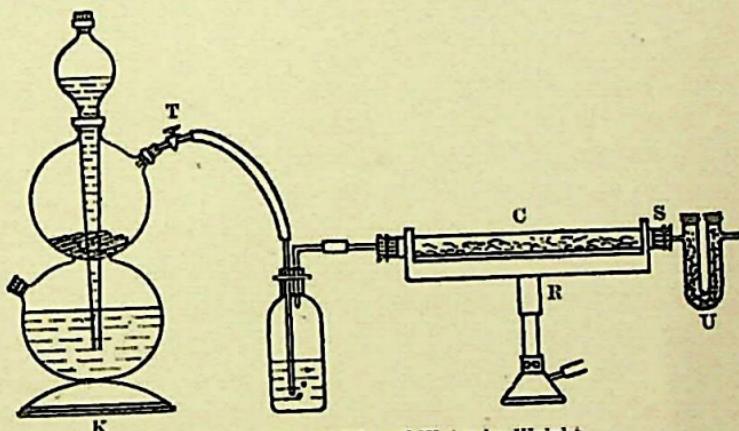
Fig. 46.—Composition of Water by Weight

tube on the Ramsay burner R (fig. 46), and light the burner. Heat the copper oxide, gently at first and then more strongly. Meanwhile pass a current of dry air over the heated copper oxide by means of the aspirator. After heating for about ten minutes, turn off the burner. Wait until the combustion-tube is cool, and then turn off the aspirator. Remove the combustion-tube from the burner.

Immediately plug the ends of the combustion-tube with two solid stoppers. This will prevent the copper oxide from absorbing moisture from the air.

Weigh the combustion-tube and its contents. (Weight = a grm.)

Fill the U-tube (U, fig. 46) with granular calcium chloride. Fit the side-tubes (a b, fig. 22) with pieces of rubber tubing

plugged with short lengths of solid glass rod. This will prevent the calcium chloride from absorbing moisture from the air.

Weigh the U-tube without the rubber and glass plugs. (Weight $= b$ grm.) Replace the plugs immediately after weighing.

Arrange the apparatus as in the diagram (fig. 46). Notice that the side-tube of the U-tube ends flush with the inside of the stopper s. Otherwise the water formed would be trapped here.

K is a Kipp's (or other) apparatus for preparing hydrogen.

D is a drying-bottle containing sulphuric acid.

The next step is to make and collect the water.

Turn on the tap T and allow a slow stream of hydrogen to pass through the apparatus. Bubbles of hydrogen should pass through D at the rate of about four per second. When the air has been swept out of the apparatus by the hydrogen, light the burner and heat the copper oxide, gently at first and afterwards more strongly. Take care not to burn the stoppers, but keep the end s of the combustion-tube so hot that steam does not condense there. After heating the copper oxide for about ten minutes, remove the burner and allow the reduced copper to cool in a very slow current of hydrogen. When the combustion-tube is cool, turn off the tap T. Remove the U-tube and the combustion-tube, and close the ends as before, using the same stoppers. Weigh the U-tube and its contents without the plugs of rubber and glass. (Weight $= c$ grm.)

The increase in weight of the U-tube gives us the weight of water produced. (Weight of water $= (c - b)$ grm.) Weigh the combustion-tube. (Weight $= d$ grm.) The decrease in weight of the combustion-tube gives us the weight of oxygen used. (Weight of oxygen $= (a - d)$ grm.) Hence the weight of hydrogen which combines with $(a - d)$ grm. of oxygen to form $(c - b)$ grm. of water is $(c - b) - (a - d)$ grm. From this we can calculate the percentage composition of water as in the example below.

Example—

Weight of combustion-tube + copper oxide $\left\{\begin{array}{l}\text{before}\\\text{reduction}\end{array}\right\}$ = 45·73 grm. (a).

| | | | | $\left\{\begin{array}{l}\text{after}\\\text{reduction}\end{array}\right\}$ = 44·87 | „ | (d). |
| „ | „ | „ | „ | | | |

„   oxygen   =   ·86 „ $(a-d)$.

„   U-tube before absorption of water   = 60·43 „ (b).

„   „   after   „   „   = 61·40 „ (c).

„   water   =   ·97 „ $(c-b)$.

$(c-b)$ grm. of water contain $(a-d)$ grm. of oxygen.

$$100 \qquad \text{„} \qquad \text{„} \qquad \frac{a-d}{c-b}\times 100 \text{„} \qquad \text{„}$$

Hence weight of hydrogen = ·97 − ·86 = ·11 grm.

·97 grm. of water contain ·86 grm. of oxygen.

∴ 100 „   „   „   88·6 „   „

Also 100 „   „   „   11·4 „ of hydrogen.

Wt. of   Wt. of
i.e. O : H = 88·6 : 11·4 = 8 : 1 approximately.

We have just shown that water consists of approximately 8 parts by weight of oxygen to 1 part by weight of hydrogen.

There is one point in the experiment as just described to which we have paid no attention; that is, the impurity of the hydrogen used. Hydrogen, as we have obtained it, contains small quantities of other gases, and these also affect the copper oxide. This experiment is of such importance that it has been performed many times, every possible precaution being taken to ensure an accurate result. The hydrogen was purified by passing it through several solutions which were chosen to absorb the impurities. It was then dried. The experiment was repeated many times, and the average of nineteen results gave the value:—

O, 88·864 per cent; H, 11·136 per cent;
or O : H as 8 : 1·002.

We conclude, then, that water consists of: (a) 2 volumes of hydrogen combined with 1 volume of oxygen, or (b) 1 part by weight of hydrogen combined with 8 parts by weight of oxygen.

History.—In very early times it was believed that earth,

air, fire, and water were the four fundamental substances out of which everything in the universe was composed.

It was also believed that water could be transformed into "earth" and into "air" (gas).

The belief that water could be changed into earth was held down to the eighteenth century. Lavoisier killed the belief by an experiment he performed about 1770. He kept water at its boiling-point in a closed glass vessel for a long time. Some "earth" (solid) was produced. This was the so-called change of water into earth.

Lavoisier showed (i) that the *whole apparatus* weighed the same after the production of the "earth" as it did before;

(ii) that the glass vessel had suffered a loss in weight exactly equal to the weight of the "earth" produced.

The only conclusion was that the "earth" was not changed water, but part of the glass vessel dissolved by the water.

In 1781 J. Priestley exploded a mixture of hydrogen and oxygen in a closed vessel. Henry Cavendish was present at the demonstration, and noticed the dew which formed inside the vessel. He determined to investigate this phenomenon. His conclusive experiment on the matter was the one which we illustrated in Experiment 42. He was thus able to show that water is a compound of hydrogen and oxygen. Cavendish communicated this most important fact to Lavoisier in 1783.

Then it was that Lavoisier named the "inflammable gas" obtained from iron and sulphuric acid "hydrogen", which means "water producer" (see p. 61). Lavoisier saw in the discovery of Cavendish the true explanation of many reactions which were at that time misunderstood. He was thus able to explain—

(i) The production of hydrogen when steam is passed over red-hot iron (see Experiment 39 (iii)).

(ii) The production of water when hydrogen is passed over heated metallic oxides (see p. 78).

(iii) The production of hydrogen when metals dissolve in acids (see pp. 59 and 83). Previously it was believed that the hydrogen came out of the metal.

The very exact determination of the composition of water by weight (p. 73) was due to Dumas in 1843.

QUESTIONS ON CHAPTER VII

1. Describe two different methods of proving the composition of water. What are the chief physical properties of water? (O. L.)

2. Describe the changes which occur when a current of coal-gas is passed over heated copper oxide. How would you collect and identify the products experimentally? (C. L.)

3. How would you bring about the combination of hydrogen and oxygen? Give some account of the compound produced. (C. L.)

4. When a metal dissolves in an acid, does the hydrogen set free come from the acid or from the metal? Give reasons for your answer.

5. Describe the preparation and properties of hydrogen.

6. How would you proceed in order to obtain a sample of copper from copper oxide?

CHAPTER VIII

ANALYSIS AND SYNTHESIS—ELEMENTS, COMPOUNDS, AND MIXTURES—OXIDATION AND REDUCTION— LAW OF CONSTANT PROPORTIONS

Analysis and Synthesis.—In our determination of the composition of water (see Experiments 42 and 45) we built up water from hydrogen and oxygen. Such a building up of a substance from its constituents is termed *synthesis*. The reverse process, that of breaking down a substance into its constituents, is termed *analysis*. Thus the analysis of water means the decomposition of water into hydrogen and oxygen (see Experiment 43).

Lavoisier synthesized mercuric oxide when he heated mercury in air and formed mercuric oxide. He analysed mercuric

oxide when he heated the mercuric oxide and obtained mercury and oxygen (see p. 45).

Elements.—When we try to analyse hydrogen we fail to get from it anything but hydrogen.

Similarly, from oxygen by analysis we can get nothing but oxygen. Hydrogen and oxygen are for this reason called *elements*.

An element is a substance which no chemist has yet succeeded in decomposing into two or more different kinds of matter.

Compounds and Mixtures.—Imagine a vessel filled partly with hydrogen and partly with oxygen, and a second vessel filled with water.

We know that water consists of hydrogen and oxygen, so that both vessels contain the same elements. The contents of the two vessels are, however, very different from one another. They differ from one another in these particulars:

(*a*) The smallest particle of water is exactly similar to every other particle. We say *the water is homogeneous*.

The hydrogen and oxygen do not form a homogeneous substance. A sample of the gas from the top of the vessel will be mainly hydrogen. A sample from the bottom will be mainly oxygen. Why?

(*b*) *The water has a constant composition* of 8 grm. of oxygen to 1 grm. of hydrogen, but the hydrogen and oxygen in the other jar may be in any proportion.

(*c*) The density of the hydrogen and oxygen mixture is the average of the densities of the hydrogen and oxygen; but not so with the water.

(*d*) If the vessel containing the hydrogen and oxygen is porous, the hydrogen and oxygen will gradually escape, but the hydrogen will escape more rapidly than the oxygen. We say that the hydrogen and oxygen can be separated by mechanical means; in this case they are separated by diffusion. (See p. 30.) *The water cannot be separated* into hydrogen and oxygen *by diffusion or by any of the other mechanical means.*

(*e*) When the hydrogen and oxygen are mixed together they do not get any warmer. *When hydrogen and oxygen are*

made to unite and form water—as in the burning of hydrogen in air or exploding hydrogen and oxygen in the eudiometer— *heat is developed.*

For these reasons we speak of the hydrogen and oxygen in the jar as a *mixture* of the two gases, but we say water is a *compound* of hydrogen and oxygen.

DISTINCTIONS BETWEEN COMPOUNDS AND MIXTURES

COMPOUNDS.	MIXTURES.
The constituents are combined in definite proportions.	The constituents may be mixed in varying proportions.
The constituents cannot be separated by mechanical means.	The constituents *can* be separated by mechanical means.
The substance is homogeneous.	The substance is heterogeneous.
The substance has its own distinctive properties.	The substance has the properties of its constituents.
Heat changes usually occur during the formation of a compound.	Heat changes do *not* occur when substances are mixed.

Experiment 46.—(i) To make a mixture of iron and sulphur.

Grind together in a mortar a few iron filings and a little sulphur. Spread out a little of the mixture on a sheet of white paper and examine it to see whether the separate particles of sulphur and iron can be distinguished. Is the mixture homogeneous?

Draw a magnet through the mixture and see whether the magnet will collect the iron, leaving the sulphur on the paper. Can the mixture be separated by mechanical means?

Place a little of the mixture in a test-tube and pour on it 1 cu. cm. of carbon bisulphide.[1]

[1] Keep the carbon bisulphide away from any flame, as the vapour is very inflammable; it is also very poisonous.

Shake up the contents of the test-tube and filter off the iron filings. Collect the filtrate and place it in a fume chamber or in the open air. When the carbon bisulphide has evaporated, notice the crystals of sulphur left in the dish. Sketch one of them.

(ii) To make a compound of iron and sulphur (iron sulphide).

Place a little of the mixture of iron and sulphur in a hard-glass test-tube, and heat the tube in the Bunsen flame.

Continue to heat it until the excess of sulphur burns away. Break the test-tube and examine the substance left.

Is the substance homogeneous?

Try to separate the constituents by mechanical means.

Oxidation.—We have seen that when copper is heated in air or oxygen it unites with the oxygen and forms copper oxide. We use the term *oxidation* to denote this process of combination of an element or compound with oxygen.

Other examples of oxidation already studied are given below.

Iron is oxidized to iron oxide when it rusts. Lead is partly oxidized to lead oxide when it is heated in air.

Magnesium is oxidized to magnesium oxide when it burns in oxygen.

Reduction.—When hydrogen is passed over heated copper oxide the copper oxide loses its oxygen, and copper is obtained (Experiment 44). We use the term *reduction* to denote this process of the removal of oxygen from a compound. Similarly, if hydrogen be passed over heated iron oxide, lead oxide, or tin oxide, the oxide is reduced and the metal obtained.

Oxidation and Reduction.—The two processes, oxidation and reduction, always occur together.

When hydrogen reduces copper oxide to copper, the hydrogen itself is oxidized to water.

Substances which are able to bring about oxidation are called *oxidizing agents*.

Substances which are able to bring about reduction are called *reducing agents*.

Law of Constant or Definite Proportions.—(i) We have seen in Experiment 45 that the water we made from hydrogen and oxygen was composed—according to our determination—of very nearly 8 parts by weight of oxygen and 1 part by weight of hydrogen. It was stated in the same chapter that when the experiment was performed with greater skill and more accurate apparatus the proportions were found by Dumas to be almost exactly $8:1$ (exactly $8:1 \cdot 002$), and later by another experimenter to be $8:1 \cdot 007$.[1]

We have seen, also, Experiment 42, that water can be formed by exploding 2 volumes of hydrogen with 1 volume of oxygen. A litre of oxygen is known to weigh sixteen times as much as a litre of hydrogen, so that if the 2 volumes of hydrogen weigh, say, 1 grm., the 1 volume of oxygen will weigh 8 grm. Thus it appears that the water made by different experimenters in different ways has a constant composition of 8 parts by weight of oxygen and 1 part by weight of hydrogen.

(ii) Magnesium oxide can be made by oxidizing magnesium by means of oxygen or nitric acid. If the experiment is carefully performed it is found that, no matter how it is made, magnesium oxide always consists of $12 \cdot 16$ parts by weight of magnesium combined with 8 parts by weight of oxygen.

(iii) We find the same constant composition in every pure substance that has been analysed, and believe the rule to be universally true.

We express this belief in what is called the *Law of Constant Proportions: a particular compound always contains the same elements combined in the same proportions.*

Perform the two following experiments, which further illustrate the law of constant or definite proportions.

Experiment 47.—To find the percentage of oxygen in potassium chlorate.

[1] The slight difference between the two values obtained, $8:1 \cdot 002$ and $8:1 \cdot 007$, is attributed to the errors necessarily present in even the most perfect experiment, and not to any difference in the composition of the water.

Weigh a clean, dry crucible with its lid. Place about a gramme of potassium chlorate in it, and weigh the crucible and its contents. By subtraction obtain the weight of potassium chlorate. Stand the crucible containing the potassium chlorate on a pipe-clay triangle supported on a tripod over a Bunsen burner, and cover the crucible with its lid. Heat the crucible strongly for about ten minutes. Allow the crucible and its contents to cool, and weigh them again. Heat the crucible again for a few minutes, and after allowing it to cool see whether any further loss in weight has occurred. If it has, the heating must be repeated. When no further loss in weight occurs on heating, the whole of the oxygen will have been expelled from the potassium chlorate. Find the weight of oxygen expelled, and calculate the percentage of oxygen in potassium chlorate as in the following example :—

Example—

Weight of crucible and lid $\qquad = 19 \cdot 22$ grm.
„　　　„　　　+ potassium chlorate $\quad = 20 \cdot 09$ „
„　　　„　　　+ residue after heating $= 19 \cdot 75$ „
Weight of potassium chlorate $\qquad = \quad \cdot 87$ „
„　　oxygen $\qquad\qquad\qquad = \quad \cdot 34$ „
$\cdot 87$ grm. of potassium chlorate contain $\cdot 34$ grm. of oxygen.
100 grm.　　　„　　　　„　　　„　$\dfrac{\cdot 34 \times 100}{\cdot 87} = 39 \cdot 1$ grm. of oxygen.

Percentage of oxygen in potassium chlorate $= 39 \cdot 1$.

It is found that pure potassium chlorate, no matter how it has been prepared, always contains 39 per cent of oxygen.

Experiment 48. — Determine the percentage of oxygen in magnesium oxide.

Place about $\cdot 5$ grm. of magnesium ribbon in a weighed crucible with a lid. Weigh the crucible and its contents, and then heat it as in fig. 23.

Every minute raise the crucible lid for a few seconds. This will allow fresh air to come into contact with the magnesium. When the magnesium no longer glows on raising the lid,

remove the lid and continue the heating for five minutes.   A little of the magnesium may have combined with some of the nitrogen in the air, forming magnesium nitride.   Add a drop of water to the contents of the crucible when cold, and heat the crucible again to convert any magnesium nitride present into magnesium oxide.

When the weight of the crucible and its contents is constant, find the weight of the magnesium oxide, and calculate the percentage of oxygen in it.

It is found that pure magnesium oxide, no matter how prepared, contains 40 per cent of oxygen.

Air, a Mixture.—The law of constant proportions is an important test in deciding whether a substance is a mixture or a compound.

Let us apply it to decide whether the air is a mixture or a compound of oxygen and nitrogen.

Careful experiment has shown that the percentage of oxygen in the air varies from $20 \cdot 97$ per cent to $20 \cdot 84$ per cent.   The difference is very little, but it is too great to be attributed to experimental error.   We must conclude then that *air has not got a constant composition*, and therefore is not a chemical compound.

This view is supported by the following facts:—

(*a*) A mixture of nitrogen and oxygen in the proportions in which they occur in air has all the properties of air.

(*b*) When such a mixture is made there is no change in temperature of the gases. ·

(*c*) Air can be changed to a liquid by cooling it and then compressing it.   If liquid air is allowed to evaporate, the nitrogen evaporates more quickly than the oxygen.   Thus the constituents of air can be separated by mechanical means.[1]

Another mechanical separation is given in Experiment 66, p. 106.

(*d*) See p. 107.

[1] Oxygen is now manufactured from air by this method.

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QUESTIONS ON CHAPTER VIII

1. What is the difference between a mixture and a chemical compound? How could you prove that air is a mixture and water a chemical compound? (O. L.)

2. Why do we believe that lead is an element?

3. Describe in detail any experiment you have seen or have performed in the laboratory to illustrate the law of combination in definite proportions. (C. L.)

4. What are the chief points of difference between mixtures and compounds? Give what reasons you can for believing that the oxygen and nitrogen in the air are not chemically combined. (C. L.)

CHAPTER IX

ACIDS, BASES, AND SALTS — EFFECT OF ACIDS ON METALS — CARBON DIOXIDE: ITS PREPARATION AND PROPERTIES.

The Effect of Acids upon some Common Metals.

NOTE.—*In using acids great care must be taken.*

If a concentrated acid be allowed to fall on the skin it may produce a painful burn. Either concentrated or dilute acid, if allowed to fall on cloth, will burn a hole in the cloth. If any acid *should* get on your skin, wash it off instantly with plenty of water. If any acid should fall on your clothes, sponge the cloth at once with strong ammonia, and then wash it with water.

When diluting concentrated sulphuric acid, always add the *acid to the water*, never the water to the acid, or the heat which is generated may cause the expulsion of drops of acid from the vessel, probably into your face.

Experiment 49.—To study the effect of acids upon some common metals.

Place about 3 cu. cm. of dilute sulphuric acid in a test-tube; add a few pieces of copper turnings. If the acid has no action on the copper, warm the test-tube and its contents over the flame of the Bunsen burner.[1]

If effervescence (bubbling due to the evolution of a gas) takes place, loosely close the end of the test-tube for a minute with your finger to imprison the gas, and then hold the open end of the test-tube close to the flame of the Bunsen burner. The result should enable you to tell whether hydrogen is given off or not. If the gas is not hydrogen, cautiously smell it and try to identify it.

Try, next, the effect of copper on *concentrated* sulphuric acid. Use only about half a cubic centimetre of concentrated acid.

Repeat the experiment, using magnesium, iron, tin, lead, and zinc with (*a*) sulphuric acid, (*b*) hydrochloric acid, (*c*) nitric acid, both dilute and concentrated.

Record the results of your experiments in tabular form as below:—

METAL.	Sulphuric Acid.				Hydrochloric Acid.				Nitric Acid.			
	Cold.		Hot.		Cold.		Hot.		Cold.		Hot.	
	Dil.	Conc.	Dil.	Conc.	Dil.	Conc.	Dil.	Conc.	Dil.	Conc.	Dil.	Conc.
Copper ...												
Magnesium												

You should now verify the following general statements from your table of results:—

When *hydrochloric acid* acts on a metal, *hydrogen* is evolved.

When *dilute sulphuric acid* acts on a metal, *hydrogen* is evolved.

[1] When heating a substance with an acid in a test-tube, always point the test-tube away from yourself and your neighbour, for fear the contents spurt out of the tube. Hold the test-tube by means of a test-tube-holder (see fig. 21, A).

When *concentrated sulphuric acid* acts on a metal, *sulphur dioxide* is evolved.

When *nitric acid* acts on a metal, *reddish-brown fumes* are evolved; except in the case of *magnesium*, which with cold dilute nitric acid gives *hydrogen*.

ACIDS, BASES, AND SALTS

Experiment 50.—To find the properties common to sulphuric acid, hydrochloric acid, nitric acid, and phosphoric acid.

Pour about 1 cu. cm. of concentrated sulphuric acid into a test-tube. Notice as you do so whether it fumes or not. Cautiously smell the acid and try to remember the smell. Pour one drop of the acid on a waste piece of paper or cloth. Notice that the cloth or paper is eaten away by the acid. The acid is said to be *corrosive*. Dip a piece of blue litmus-paper in the acid and notice the effect of the acid on the colour. Dilute the acid by pouring it into an equal volume of water in another test-tube. Add sodium hydroxide (caustic soda) drop by drop to the acid until a piece of blue litmus-paper placed in the acid turns purple. Evidently we have destroyed the acid properties of the liquid. We are then said to have *neutralized* the acid.

Pour the solution into an evaporating-dish. Place the dish on a wire gauze on a tripod. Boil the solution by means of a Bunsen burner to concentrate it. Dip a glass rod into the solution, withdraw it, and allow it to cool. When, on cooling, the glass rod is found to be coated with a solid substance in the form of crystals, place the dish on the bench and allow the solution to cool. Notice the appearance of the solid which separates out in the form of crystals. We call the solid obtained a *salt*.

Repeat the experiment, using hydrochloric, nitric, and phosphoric acids, both concentrated and dilute.

From the results of this experiment and Experiment 49 fill in the table below.

Acid.	What Effect has the Acid on Blue Litmus?	Can Hydrogen be set free from the Acid by Means of a Metal?	Is the Acid Corrosive?
Sulphuric acid ...			
Hydrochloric acid			
Nitric acid ...			
Phosphoric acid ..			

Experiment 51.—To determine whether a metal will neutralize an acid.

We will try zinc and sulphuric acid.

Take the liquid remaining in the flask after the preparation of hydrogen from zinc and sulphuric acid. Pour about 10 cu. cm. of it into an evaporating-dish, and add pieces of zinc until no further effervescence takes place. Test the liquid with red and blue litmus-papers. Is it neutral?

Concentrate the solution and try to obtain crystals of the salt produced. The experiment should be repeated with other metals and acids. Iron and sulphuric acid, lead and nitric acid, and magnesium and hydrochloric acid are suitable.

Experiment 52.—To determine whether a basic oxide will neutralize an acid and form a salt.

We will try copper oxide and sulphuric acid.

Pour about 25 cu. cm. of dilute sulphuric acid into an evaporating-dish standing on a gauze on a tripod. Add black copper oxide little by little until some remains undissolved. Boil and stir the solution. Filter it and test the clear-blue solution with litmus. Is it neutral? Try to obtain crystals of the salt produced. This experiment should be repeated with other basic oxides and acids. Lead oxide (litharge) and nitric acid, zinc oxide and sulphuric acid, and copper oxide and hydrochloric acid are suitable substances.

Do *all* the oxides tested neutralize the acid used?

We call *all* the solids formed by the interaction of the various acids and basic oxides, salts.

We are now in a position to say *what we mean by an acid*, although to give a really satisfactory definition of an acid is perhaps beyond our powers at this stage.

Acids are substances which usually—

    (*a*) *have a sour taste,*
    (*b*) *are corrosive,*
    (*c*) *change blue litmus red;* and always
    (*d*) *contain hydrogen, part or all of which can be replaced by a free metal, or the metallic part of an oxide or hydroxide.*

No *one test* is sufficient to decide whether a substance is an acid or not.

Alum has properties (*a*), (*b*), and (*c*); but it is not classed as an acid.

Copper sulphate has property (*c*); but it is a salt.

Caustic soda contains hydrogen which is replaceable by the metals aluminium and zinc; but it is a hydroxide.

We have spoken of the solid produced when an acid is (*a*) neutralized by a hydroxide, (*b*) neutralized by a metal, (*c*) neutralized or acted upon by a basic oxide, as a salt.

A salt is the substance produced by replacing all, or part, of the hydrogen of an acid by a metal.

Thus when the *metal* zinc neutralizes sulphuric acid, the hydrogen replaced by the zinc comes off as a gas. When the basic *oxide*, zinc oxide, is used to neutralize sulphuric acid, the hydrogen replaced by the metal does not come off as a gas, but unites with the oxygen in the oxide to produce water.

Hydroxides, which are basic oxides + water, act similarly to basic oxides—water instead of free hydrogen is produced.

We have seen that acids can be neutralized by (*a*) metals, (*b*) basic oxides, (*c*) hydroxides.

The term **base** is used to include all basic oxides and hydroxides.

A base is a substance which reacts with an acid to form a salt and water.

We have further seen that the hydroxides of sodium, potassium, and in a lesser degree calcium and magnesium

hydroxides are soluble in water.   They also possess detergent and soapy properties.

The name **alkalis** *is given to these soluble hydroxides.*

It will be gathered from what has been said that **an acid reacts with a base to form a salt and water.**   This is not the only method of preparing salts.   We have already prepared the salt zinc sulphate by the action of a *metal* on an acid.

How the Salts are named.   If the acid used is—

sulphuric acid,	the salt is called a		*sulphate.*
hydrochloric ,,	,,	,,	*chloride.*
nitric ,,	,,	,,	*nitrate.*
phosphoric ,,	,,	,,	*phosphate.*

We indicate the metal present in the base, which is combined with the acid to form the salt, by prefixing it to the name of the salt.   Thus—

zinc oxide and sulphuric acid form *zinc* sulphate and water.

copper ,,	,,	,,	*copper*	,,	,,
sodium hydroxide ,,		,,	*sodium*	,,	,,

lead oxide and hydrochloric acid form *lead* chloride and water.

magnesium oxide	,,	,,	,,	*magnesium*	,,	,,

History.—*Acids.*—Up to about the year 1780 oxygen was thought to be the essential element in all *acids.*   This belief was due to Lavoisier.   It arose from the fact that an anhydride unites with water to form an acid.   (See p. 51.)

Hydrochloric acid was then supposed to contain oxygen. In 1810 Davy showed that hydrochloric acid does *not* contain oxygen.   This proved Lavoisier's theory of acids to be wrong.

Since then it has been shown that hydrogen, not oxygen, is the essential element in all acids.

Salts.—In early times all soluble substances which had a salty taste were called *salts.*   Many substances which are not salts came under this definition, and were wrongly called salts.

By the seventeenth century a clearer idea of a salt had been reached.   Only substances formed by the interaction of acids and alkalis were then called salts.

The present-day idea that a salt is formed when a base neutralizes an acid only dates back to the year 1745.

THE ACTION OF ACIDS ON LIMESTONE AND SODA— CARBON DIOXIDE: ITS PREPARATION AND PROPERTIES.

Experiment 53.—To find the action of the common acids upon (i) limestone, (ii) washing-soda.

(i) Place a few small pieces of limestone in a test-tube, and add a few drops of dilute hydrochloric acid. Notice the effervescence that takes place. Dip a piece of glass rod into some clear lime-water. Hold the rod, with a drop of lime-water hanging from the end, well inside the test-tube, but not touching the liquid. Notice whether there is any change in the appearance of the lime-water. Next hold a piece of wet blue litmus-paper over, but not in contact with, the mouth of the test-tube. Is the escaping gas acid or alkaline? What gas is given off when hydrochloric acid acts upon limestone?

Repeat the experiment, using (*a*) dilute sulphuric acid, (*b*) dilute nitric acid.

(ii) Proceeding exactly as in (i), find the effect of (*a*) hydrochloric acid, (*b*) sulphuric acid, (*c*) nitric acid, upon washing-soda and any other carbonates or bicarbonates available.
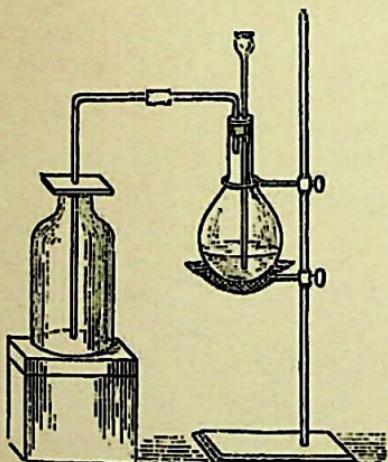
Fig. 47.—Preparation of Carbon Dioxide from Marble by means of Hydrochloric Acid

Experiment 54.—To prepare carbon dioxide and to examine its properties.

(i) Use the apparatus shown in fig. 47, or that depicted in fig. 39. Carefully slide a few small pieces of marble, chalk, or limestone down the neck of the flask. Insert the stopper and then cover the limestone with dilute hydrochloric acid. Collect the gas over water as in fig. 39, or, since the gas is

somewhat soluble in water, collect it by downward displacement of air (fig. 47). The gas-jar contains air only, and the delivery-tube reaches to the bottom of the jar. The top of the gas-jar is covered with a sheet of paper, which is pierced by a hole to allow the delivery-tube to enter. The paper prevents, to some extent, the carbon dioxide from passing out into the air, and the air from passing into the gas-jar.

This method of collecting is practicable only with heavy gases. The heavy carbon dioxide will displace the air and fill the gas-jar much the same as a liquid would.

To tell when the jar is full of carbon dioxide the paper covering the jar should be raised, and a lighted match should be held near the mouth of the jar. If carbon dioxide is overflowing from the jar the match will be extinguished. When the jar is full of the gas, cover it with a greased plate, and collect four more jars full of the gas in a similar manner, adding more acid when the gas ceases to come off.

Fig. 48.—Pouring Carbon Dioxide downwards

(ii) Examine the gas according to the scheme given in Appendix I.

Perform the following additional experiments with the jars of carbon dioxide collected:—

(a) Try to burn magnesium in the gas (fig. 35), proceeding as in Experiment 35 (vi). Afterwards examine the products of the reaction carefully for black particles mixed with the white powder which is formed.

(b) Shake up a jar full of the gas with lime-water, and note the effect of the gas on the lime-water.

(c) Dip the end of the delivery-tube into a test-tube half-full of lime-water, diluted with water, and allow the carbon dioxide from the apparatus (fig. 47) to bubble slowly through

the lime-water. Notice the changes in appearance of the lime-water. Boil the clear solution, cool it, and add dilute hydrochloric acid to it. Test the gas evolved on the addition of the acid with lime-water.

(*d*) Try to pour the carbon dioxide from one jar into a jar full of air exactly as you would pour water from one vessel into another (fig. 48). Test both jars for carbon dioxide.

Keep some of the liquid remaining in the flask for Experiment 56. Make a list of the properties of carbon dioxide.

Properties of Carbon Dioxide.—Carbon dioxide is an invisible gas with a sharp taste. It is heavier than air. It will not support combustion. It is fairly soluble in water,[1] forming an acid solution. When heated in contact with magnesium, carbon dioxide is decomposed, forming magnesium oxide and carbon. The metals sodium, potassium, and calcium affect the gas similarly.

The fact that carbon dioxide is a heavy gas may

Fig. 49.—Carbon Dioxide is heavier than Air

be strikingly shown as follows:—

A beaker is hung from one arm of a balance, as in fig. 49. It is counterpoised by the addition of weights to the other scale-pan.

A jar of carbon dioxide is then poured into the beaker. As the carbon dioxide displaces the air from the beaker the beaker sinks down. This shows that the carbon dioxide weighs more than the air it displaces.

Experiment 55.—To find the effect of carbon dioxide upon a solution of caustic soda.

Use the apparatus shown in fig. 50.

Generate carbon dioxide as in Experiment 54 and pass the

[1] See Appendix II.

gas through a small quantity of a weak solution of caustic soda contained in the smaller flask.

Test the solution with blue litmus-paper to decide whether the caustic soda has been neutralized by the carbon dioxide. Continue to pass the carbon dioxide through the solution for some time.

Evaporate the solution to dryness to obtain the salt produced. Test the salt so obtained with dilute acid. (Is carbon dioxide evolved ?)

Apply the same test to a crystal of washing-soda,

Fig. 50.—Effect of Carbon Dioxide upon Caustic Soda

and compare the results obtained in the two cases.

Carbon dioxide is thus seen to be very soluble in caustic soda, forming sodium carbonate (washing-soda).

$$\left.\begin{array}{c}\text{carbon} \\ \text{dioxide}\end{array} + \begin{array}{c}\text{sodium} \\ \text{hydroxide}\end{array}\right\} \text{form} \left\{\begin{array}{c}\text{sodium} \\ \text{carbonate}\end{array} + \text{water}.\right.$$

The solution of carbon dioxide in water may be looked upon as carbonic acid. Sodium hydroxide is a base, and the union of the base and the acid forms a salt (sodium carbonate) and water. Similarly, when lime-water (calcium hydroxide) is used as a test for carbon dioxide, a salt is formed by the union of the acid and the base.

$$\left.\begin{array}{c}\text{carbon} \\ \text{dioxide}\end{array} + \begin{array}{c}\text{calcium} \\ \text{hydroxide}\end{array}\right\} \text{form} \left\{\begin{array}{c}\text{calcium} \\ \text{carbonate}\end{array} + \text{water}.\right.$$

The calcium carbonate thus formed causes the "milkiness" of the solution. If excess of carbon dioxide be passed through the solution, the calcium carbonate unites with the carbon dioxide and forms calcium bicarbonate.

carbon dioxide + water form carbonic acid.

carbonic acid + calcium carbonate form calcium bicarbonate.

Similarly with caustic soda, excess of carbon dioxide converts the sodium carbonate into sodium bicarbonate (baking-soda).

carbon dioxide + water form carbonic acid.

              carbonic acid + sodium carbonate form sodium bicarbonate.

There are thus two classes of carbonates:

(i) The *normal carbonates* like sodium carbonate. In these *all* the replaceable hydrogen in the acid has been replaced by the metal.

(ii) The *acid carbonates*[1] like sodium bicarbonate. In these only part of the replaceable hydrogen in the acid has been replaced by the metal.

Because carbonic acid forms two classes of salts it is called a *di-basic acid.*

Similarly, by the addition of caustic soda to sulphuric acid two different sulphates can be formed.

(*a*) With a certain weight of caustic soda and a given weight of sulphuric acid all the hydrogen in the sulphuric acid is replaced by the sodium, and *normal sodium sulphate* is formed.

(*b*) With half this weight of caustic soda, and the same weight of sulphuric acid as was employed before, only half the hydrogen in the sulphuric acid is replaced by the sodium, and *acid sodium sulphate* is formed.

Therefore sulphuric acid is a di-basic acid.

Phosphoric acid forms three different salts on treatment with caustic soda. It is therefore said to be *tri-basic.*

Experiment 56.—To examine the salt produced when hydrochloric acid acts upon limestone.

Take some of the solution kept from Experiment 54. Evaporate the solution to dryness. Leave the dry solid exposed to the air, and notice that it absorbs moisture and becomes quite wet, ultimately dissolving in the absorbed water. Such substances are said to be *deliquescent.* The substance is the salt calcium chloride, the substance which we have previously used to dry gases.

---

[1] Not all acid carbonates are acid to litmus.

Experiment 57.—To show the presence of carbon dioxide (*a*) in the atmosphere, (*b*) in expired air.

(*a*) Fit two bottles, each containing a little lime-water, with corks and two tubes, as in fig. 51. Place the tube B in the mouth and suck the air out of the bottle, or else join B to an aspirator. This will cause a current of air to pass in at A and bubble through the lime-water. Continue the suction until the lime-water turns milky.
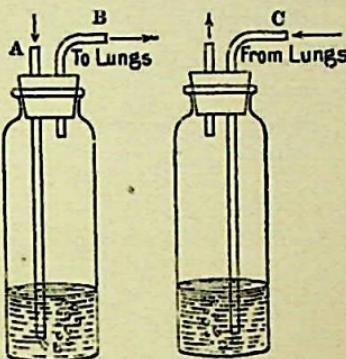
Fig. 51.—Presence of Carbon Dioxide in Air

(*b*) Blow through C into the lime-water, and notice that it turns milky much sooner than it did in (*a*). What does this indicate?

We must now include carbon dioxide in the constituents of the atmosphere. The usual percentage of carbon dioxide in the atmosphere is about ·04 per cent. The quantity varies in different places, since the gas is expired both by plants and animals. It is also absorbed, as food, by the green parts of plants, so that the proportion remains fairly constant. The gas is poisonous, as it prevents the blood from absorbing the necessary quantity of oxygen from the air during respiration.

QUESTIONS ON CHAPTER IX

1. What reactions may take place on passing carbon dioxide through lime-water?

2. Working with sulphuric acid, nitric acid, caustic soda, and calcium hydroxide, how many salts could you prepare? State briefly how you would prepare each of them.

3. What properties must a substance possess to be described as an acid? Quote any instances you can of acids being formed from oxides. (O. L.)

4. Write a concise account of the characteristic properties of acids.　(C. L.)

5. Describe a method for the preparation of carbon dioxide. How does the gas react chemically with (a) lime-water? (b) caustic soda?

6. State the chief physical and chemical properties of carbon dioxide. How would you distinguish experimentally between jars of carbon dioxide, oxygen, hydrogen, and air?

7. Write a concise account of the characteristic properties of alkalis.

CHAPTER X

EXPERIMENTAL STUDY OF LIMESTONE—CHEMICAL AND PHYSICAL CHANGES

We will next make a chemical study of limestone. Our experiments will be planned with a view to determining the nature of the substance. Is it an element, a compound, or a mixture? If a compound, of what elements is it composed? We have already found that heat and electricity are powerful means of analysing compounds; we shall therefore begin by studying the effect of heat on limestone.

Experiment 58.—To find the effect of heat on limestone.

Place a little powdered limestone in a hard-glass test-tube and heat it
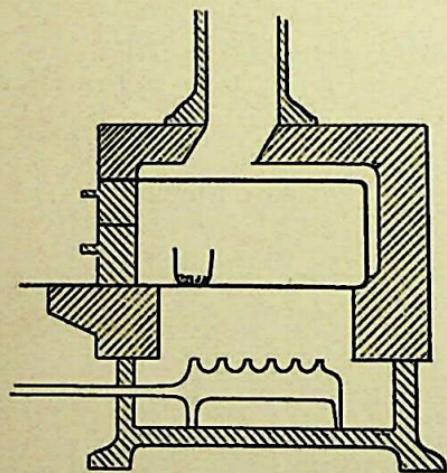
Fig. 52.—Muffle Furnace (section)

strongly in a hot Bunsen-burner flame. Test the gas given off, if any, by means of a drop of lime-water hanging from the

end of a glass rod held inside the test-tube. What gas is given off from limestone when it is heated strongly?

If more of the limestone is heated strongly in a furnace a larger quantity of carbon dioxide can be obtained. We thus see that limestone is not an element. To decide whether it is a mixture or a compound we will first see whether it obeys the law of constant proportions. One way of doing this is to drive off all the carbon dioxide contained in the

Fig. 53.—Muffle Furnace (general view)

limestone; and to do this we must use a very little limestone and heat it very strongly. The limestone contained in a crucible is generally heated in a furnace such as the muffle furnace (figs. 52 and 53), or the small furnace shown in fig. 54. With a hot Bunsen burner, however, and a spoon of silica glass the experiment may be conducted quite easily, as in the next experiment.

FIRECLAY

CRUCIBLE

Experiment 59.—To find the percentage of carbon dioxide in limestone.[1]

Weigh a clean, dry silica spoon. Into it place not more than half a gramme of powdered limestone. Weigh the spoon and its contents; obtain the weight of limestone taken. Adjust the air-hole of the Bunsen burner until the flame "roars", and hold the spoon in the hottest part of the flame

Fig. 54.—Small Furnace

[1] Different students might with advantage use limestone, chalk, and oyster shell, and the identity of these substances (chemically) be determined by collecting and discussing the results.

(fig. 55). Continue the heating until the weight is constant. (This will take about twenty minutes.)

Then find the weight of the crucible and its contents, and calculate the percentage loss in weight of limestone on heating, as in the example below. Retain the heated limestone for the next experiment.

Example—

Weight of spoon	=	2·666 grm.
„ „ + limestone	=	3·282 „
„ limestone	=	·616 „

Weight of spoon + residue after heating = 3·016 „
„ carbon dioxide expelled = ·266 „

·616 grm. of limestone contain ·266 grm. of carbon dioxide.

$\therefore 100 \quad ,, \qquad ,, \qquad ,, \quad \dfrac{·266}{·616} \times 100$ grm. of carbon dioxide

$= 43·2$ grm.

Experiment 60.—To examine the substance remaining after the carbon dioxide has been removed from limestone by heat.
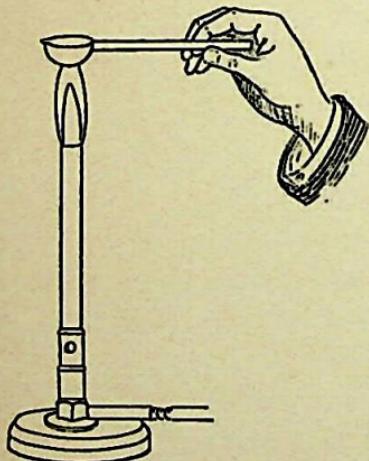
Fig. 55.—Production of Lime from Chalk

When the substance is cold add a few drops of water to it. What happens? What does this indicate? (See p. 77.) Test the substance with wet litmus-paper to see whether it is acid or alkaline.

Make a paste of the solid and water, dilute it, and filter it to obtain a clear solution.

Blow a current of carbon dioxide through the solution. (Expired air will do.)

What is the solution, and what is the solid left on heating limestone?

Add dilute hydrochloric acid to a little of the substance. Does it effervesce? Try to neutralize a little hydrochloric acid with some of the substance. Can you? What does this indicate?

We have seen that heat sets free carbon dioxide from limestone, and that limestone when strongly heated loses 44 per cent of its weight. We have assumed that this 44 per cent represents the percentage of carbon dioxide in limestone.

We have also seen that dilute acids set free carbon dioxide from limestone. If we can show that the loss in weight when an acid acts upon limestone is 44 per cent of the whole mass of limestone, this would confirm our belief that limestone contains 44 per cent of carbon dioxide.

Experiment 61.—To find the percentage of carbon dioxide set free from limestone by an acid.

The apparatus shown in fig. 56 (i) or (ii) can be used. (i) is preferable to (ii) as being less "top heavy".

D is a drying-tube containing calcium chloride.
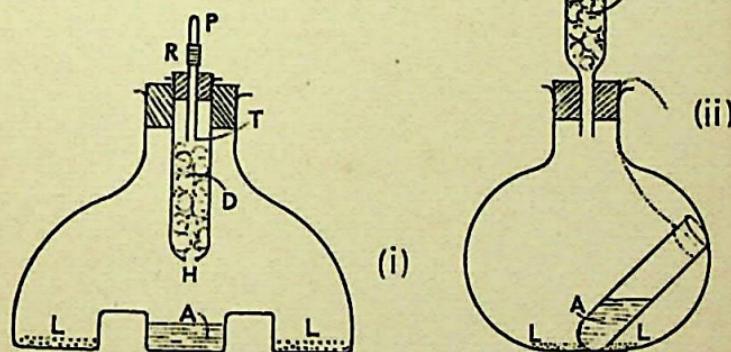
Fig. 56.—Apparatus for determining the Weight of Gas given off during a Reaction

P is a solid glass plug connected to the piece of glass tubing T by means of rubber tubing R.

A is hydrochloric acid.

L is powdered limestone.

In (ii) the acid is placed in the small test-tube, to which a piece of cotton is attached. The test-tube is then lowered into the flask (100 cu. cm.), which has a wide mouth.

In (i) the acid is introduced by means of a pipette. D contains a small hole at H for the escape of the carbon dioxide.

Remove the stopper and drying-tube from the apparatus.

Fold a narrow (3 cm.) strip of glazed paper lengthways down the centre. Weigh it. On it weigh out about 1 grm. of powdered limestone. Find the weight of limestone taken. Carefully slide the limestone down the paper into the flask at L (fig. 56).

Place about 6 cu. cm. of concentrated hydrochloric acid, diluted with 3 cu. cm. of water, into A. [Take great care that none of the acid comes in contact with the limestone. If apparatus (ii) is used, keep the outside of the test-tube dry.]

Replace the stopper and drying-tube, and weigh the whole apparatus.

Remove the plug P, and tilt the apparatus so that a few drops of the acid may flow on to the limestone. Repeat this at short intervals until no further action takes place.

Attach a piece of glass tubing to R, and suck out the carbon dioxide remaining in the flask. (Notice its taste.) Remove the glass tube, replace the plug P, and weigh the apparatus. Calculate the percentage loss in weight, as in the example below.

Example—

Weight of limestone taken	=	1·25 grm.
„ apparatus—		
(a) before carbon dioxide is set free	=	80·15 „
(b) after „ „	=	79·60 „
Weight of carbon dioxide	=	·55 „

$$\text{Percentage of carbon dioxide in limestone} = \frac{\cdot 55}{1\cdot 25}$$
$$= 44 \text{ per cent.}$$

The results of this experiment confirm our belief that limestone contains 44 per cent of carbon dioxide. The results of

Experiment 60 indicate that the remaining 56 per cent is lime. We found in the same experiment that lime is slightly soluble in water, forming lime-water, and that lime-water is turned milky by carbon dioxide. We are now in a position to understand the cause of this turbidity. It is caused by particles of limestone which are formed by the union of lime and carbon dioxide. In other words, we were analysing limestone when we heated it and split it up into lime and carbon dioxide, and we are synthesizing limestone when we use lime-water to test for carbon dioxide.

We have also seen (pp. 89 and 91) that when excess of carbon dioxide is passed through lime-water, the carbon dioxide first precipitates (throws down) the limestone and then the solution becomes clear again. This shows that a solution of carbon dioxide in water (carbonic acid) will dissolve limestone.

Limestone has now been shown to be a compound of lime and carbon dioxide.

We already know that carbon dioxide is a compound of carbon and oxygen.

The next question is, what is lime?

Lime is usually prepared by heating limestone, but it *can* be prepared by heating the metal calcium in air or burning it in oxygen. This shows that *lime is an oxide of the metal calcium, and therefore should be called calcium oxide.*

It has been shown (p. 97) that lime or calcium oxide has the properties of a base. It is therefore a basic oxide.

We know that carbon dioxide is an acid oxide which dissolves in water to form carbonic acid. *Hence limestone,* a compound of calcium oxide and carbon dioxide, *must be a salt,* and according to our scheme of naming salts must be called *calcium carbonate.* Thus:—

A Base +   an Acid   form   a Salt + Water.
Calcium   + carbon dioxide + water $\Big\}$ form $\Big\{$ calcium   + water.
  oxide   (carbonic acid)   carbonate

Finally, if carbon dioxide be passed over lime, heat is de-

veloped and calcium carbonate formed. This is additional evidence that the lime and carbon dioxide form a compound.

Lime + carbon dioxide form limestone.

We are now in a position to understand more fully the reaction which takes place when sodium or calcium acts upon water (see p. 58). The hydrogen of the water is set free, and the oxygen combines with the sodium or calcium to form sodium oxide or calcium oxide. These oxides unite with the water, forming sodium hydroxide (caustic soda) or calcium hydroxide (slaked lime). These hydroxides dissolve in the excess of water. Thus:—

(i) Sodium + water   form Hydrogen + Sodium oxide. .
        (hydrogen oxide)
(ii) Sodium oxide + water ,,   Sodium hydroxide.
or   Sodium + water   ,,   Hydrogen + sodium hydroxide.
     Potassium + water   ,,   Hydrogen + potassium hydroxide.
     Calcium + water   ,,   Hydrogen + calcium hydroxide.
     Magnesium + water   ,,   Hydrogen + magnesium hydroxide.
Generally (but only with certain metals),

    A metal + water form hydrogen + a hydroxide.

Chemical and Physical Changes.—When a piece of steel is stroked with a magnet it acquires a new property. It is then able to attract iron filings. We say the steel has been magnetized.

The steel is still exactly the same kind of material as before— it contains the same elements as before, and in the same proportions. *It has also neither increased nor decreased in weight.* The steel has all its old properties, and has in addition received a new one.

When a certain weight of water is changed into ice, or steam, the ice, or steam, still contains one-ninth of its weight of hydrogen and eight-ninths of its weight of oxygen, just as the water did. Here, again, *the ice, steam, and water weigh exactly the same.*

All the properties of the water are not possessed by the ice nor the steam. The density of ice or of steam is very different from the density of water, but by heating the ice or cooling

the steam we can get back the water again—and nothing but the water. Such changes are called *physical changes.*

When mercury is heated in oxygen it changes from a liquid into a red powder. This red powder *weighs more than the mercury from which it was produced.* The special properties which serve to distinguish mercury from all other substances are not possessed by the red powder. From the red powder oxygen can be obtained, showing that this red powder is not merely altered mercury but *a new substance* (mercuric oxide).

Such a change is spoken of as a *chemical change.*

Similarly, when limestone is heated, a chemical change occurs, because (*a*) the weight of the lime is less than the weight of the limestone from which it was produced; (*b*) the lime has properties which are quite distinct from those of limestone; (*c*) the lime differs in composition from the limestone in containing no carbon and a less percentage of oxygen.

Hence the lime is a totally different substance from the limestone.

The answer to the question as to whether a certain change is a chemical one or not depends upon the answer to the question: Has a new substance been formed? In some cases the answer to this question is fairly obvious, but in other cases it is very difficult to say with certainty.

Chemical and Physical Properties.—The properties of a substance may be divided into two groups.

There are *the properties which we observe when the substance remains unchanged.* The colour, smell, taste, density, boiling-point, and freezing-point of a substance are examples of such properties. They are spoken of as the *physical properties* of the substance.

The ability to burn in oxygen is a property of hydrogen, to demonstrate which, it is necessary to destroy the hydrogen as such, by making it unite chemically with oxygen to form a new substance—water. Similarly, the ability to support the combustion of carbon is a property of oxygen, which only becomes apparent when oxygen chemically unites with carbon to form a new substance—carbon dioxide.

The affinity of chlorine for metals and the reducing action of hydrogen are properties of these elements, to demonstrate which it is necessary to make the elements take part in a chemical change. Such properties of substances—*properties which become evident only when the substance takes part in a chemical change*—are called *chemical properties.*
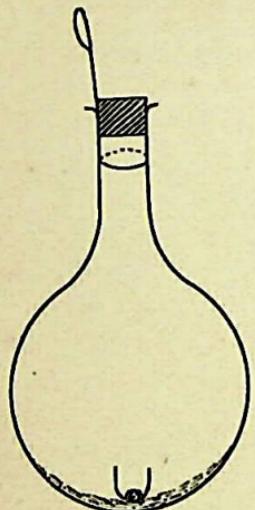
Fig. 57.—Combustion of Phosphorus in an Enclosed Space

THE CONSERVATION OF WEIGHT

Experiment 62.—Cover the bottom of a large round-bottomed flask with a layer of dry sand. Place a small piece of dry phosphorus in a small crucible, and rest the crucible on the sand. Fit the flask with a tightly-fitting rubber stopper, and weigh the flask and its contents (fig. 57).

Warm the bottom of the flask and the phosphorus will take fire. Notice that the flask becomes filled with dense white fumes (phosphorus pentoxide), and that in a short time the phosphorus is extinguished. (Why?) Allow the flask and its contents to cool, and then reweigh them.

It will be noticed that *no change of weight can be observed*, although the phosphorus and oxygen have disappeared, and a new substance, phosphorus pentoxide, has been produced.
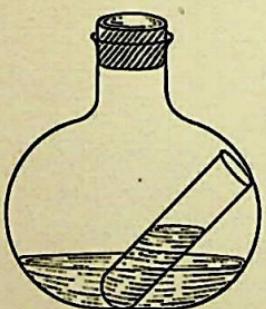
Fig. 58.—Chemical Action in an Enclosed Space

Experiment 63.—Select a wide-mouthed flask, and in it place a small test-tube (fig. 58). Place some potassium bichromate in the test-tube, and some lead acetate in the flask. Close the flask securely by means of a well-fitting rubber stopper. Weigh the flask and its contents.

Then tilt the flask to allow the potassium bichromate to mix with the lead acetate. Notice the yellow precipitate of lead chromate which forms.

When cool, weigh the flask and its contents. It will be found that although a chemical change has taken place *no change of weight can be observed.*

Experiment 62 illustrates the fact that when combustion takes place *no change of weight can be observed* provided that all the products of the combustion are weighed.

The rule just mentioned, that no change of weight can be observed, is not confined to combustion only, but is equally true of all chemical reactions. Experiment 63 illustrates this fact.

Experiments 62 and 63 may be repeated with other substances, and provided that none of the substances produced are allowed to escape, there will be no change in weight. We may summarize the results of the experience of all chemists and say: *The total weight of the substances which take part in a chemical reaction remain unaltered.*

This statement is called the **Law of Conservation of Weight** (or of matter).[1]

The distinction between "mass" and "weight" has already been alluded to (see p. 3).

The mass of a body is a measure of the amount of matter the body contains. The weight of a body is a measure of the force with which the earth attracts the body. This force depends upon the distance of the body from the centre of the earth.

Experiment and observation show that the masses of bodies are proportional to their weights. A body of twice the mass has twice the weight if weighed at the same place.

We make use of the equality of weight possessed by equal masses at the same place on the earth to compare masses by means of the balance when we "weigh" objects. For this reason, when seeking experimental confirmation of the law referred to, the weights of the reacting substances and the products must be determined at the same place.

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[1] Matter is a name given to anything which has weight.

QUESTIONS ON CHAPTER X

1. How would you show that carbon is a constituent of marble?

2. Describe the chemical changes that take place when limestone is (i) heated strongly in air, (ii) added to hydrochloric acid.

3. Describe and explain the difference in behaviour between lime and limestone when each is added to (i) an acid, (ii) water.

4. How would you proceed to show that an oyster shell and a piece of marble are both composed of the same substance?

5. Describe in detail how you would make a bottle of lime-water if you were provided with a piece of limestone.

6. Explain what is meant by (i) a physical change, (ii) a chemical change.

Is the rusting of iron a physical or a chemical change? Give reasons for your answer.

7. What do we mean by the phrase: "The conservation of matter"? Why do we believe the statement to be true?

CHAPTER XI

NATURAL WATERS

Experiment 64.—(i) To find the weight of dissolved solid contained in 100 cu. cm. of tap-water.

Proceed as in the latter part of Experiment 8, p. 12, using 50 cu. cm. of tap-water. Add nothing to the water. Notice carefully the appearance of the water from the commencement of heating until the water begins to boil.

Repeat the experiment with sea-water if available.

(ii) *To examine the solids obtained from tap-water.*[1]

Notice the white deposit left on the evaporating-dish after evaporating the tap-water to dryness.

[1] This experiment is only suitable for "hard" tap-water (see p. 110).

Get a drop of clear lime-water on the end of a glass rod ready to test for carbon dioxide. Pour a few drops of hydrochloric acid on the white deposit. Notice the effervescence which occurs. Test the gas given off with lime-water.

What does the result show about the composition of the solids dissolved in tap-water?

In Experiment 64 it has been seen that before boiling
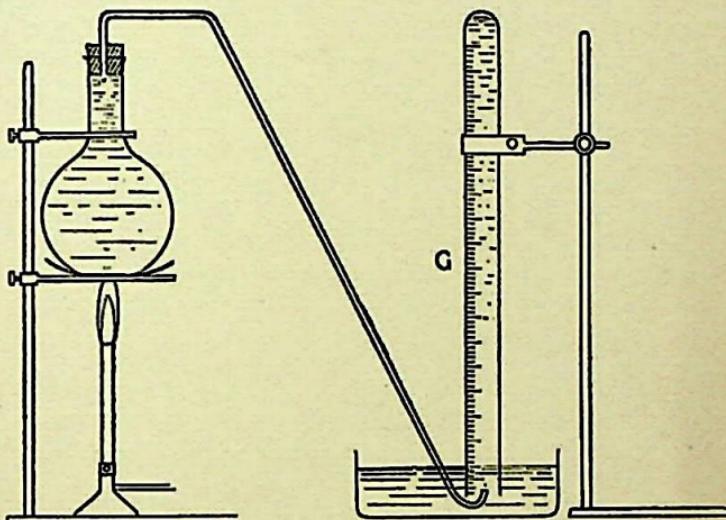
Fig. 59.—Removal and Collection of Gases dissolved in Water

commenced small bubbles of gas made their appearance on the bottom of the evaporating-dish. They then increased in size and rose to the top of the water, where they burst.

The collection of similar bubbles of gas is noticeable on the inside of a vessel of water which has been standing some time. The water then has a "flat" taste. Let us collect and examine a sample of this gas.

Experiment 65.—To determine the volume of gases dissolved in 1 litre of tap-water.

Fit up the apparatus shown in fig. 59.

Fill the 500-cu.-cm. flask quite full of water. See that the upper end of the delivery-tube is level with the bottom of the

cork. Fill the delivery-tube with water, by suction, and insert the cork into the flask. The flask and delivery-tube should now be quite full of water. Partly fill the trough with water and invert in it the graduated tube G full of water. Then place the lower end of the delivery-tube under the tube G.

Heat the water by means of a Bunsen burner, and carefully note what happens.

When all the dissolved gases have been driven out of the water, bubbles of steam will begin to pass down the delivery-tube. Notice that they are condensed by the cold water and so do not collect in G. When this occurs, remove the delivery-tube from the trough and cease heating the water in the flask.

How do you know that the gases collected have *not* come from the decomposition of water?

When the gases are cool, read the volume of gases collected. [Volume = a cu. cm.] Find the exact capacity of the flask by filling it with water and transferring the water to a measuring cylinder. [Capacity = b cu. cm.]

Then b cu. cm. of water contains a cu. cm. of dissolved gases.

∴ volume of dissolved gases in 1 litre of tap-water

$$= \frac{1000a}{b} \text{ cu. cm.}$$

Experiment 66.—To determine the percentage of oxygen in the gases dissolved in water.

Collect about 20 cu. cm. of the gases as in Experiment 65. Tightly cork the open end of the graduated tube and remove the tube from the trough. Place the tube, mouth downward, in a tall jar nearly full of water, and remove the cork. Measure the volume of the gases collected. (See Experiment 29, p. 39.)

Remove the oxygen from the gases collected by the slow combustion of phosphorus as in Experiment 31, p. 42. The phosphorus may be fastened to the end of a length of copper wire and thrust up into the gas. After some days, measure the volume of gas remaining in the tube. The decrease in volume is due to the combination of the oxygen with the phosphorus.

Calculate the percentage of oxygen in the gases dissolved in water.

The experiments just performed show that tap-water contains solids and gases in solution. At least one of the solids has been shown to be a carbonate, for it evolves carbon dioxide on the addition of dilute acid.

Similarly, one of the gases has been shown to be oxygen. This oxygen forms a percentage of the dissolved gases greater than the percentage of oxygen in the air.

On the inside of kettles and boilers these dissolved solids collect in large quantities and form the "fur" which coats the inside of the vessel.

By further examination of tap-water the following solids have been shown to be commonly present: Calcium carbonate (limestone), calcium sulphate, calcium chloride, magnesium carbonate, magnesium sulphate, and magnesium chloride.

Amongst the gases dissolved in water are oxygen, nitrogen, and carbon dioxide—the gases of the atmosphere, but they are not in the same proportions as those in which they occur in the air.

Source of the Substances in Solution in Water.

If the history of the water is considered it may be possible to account for the presence of these substances which are dissolved in tap-water.

Rain - water.—The rain, in descending, dissolves some oxygen, nitrogen, and carbon dioxide from the air. It has been shown that it dissolves a greater proportion of the oxygen than it does of the nitrogen in the air. This is one reason for asserting that air is a *mixture* (not a compound) of nitrogen and oxygen. If the nitrogen and oxygen were *combined* to form air, the two gases would go into solution in the proportions in which they occur in air.

Spring - water.—Some of the rain sinks into the soil, and if it filters through a bed of limestone, *some of the limestone will be dissolved, because the water contains carbon dioxide in solution.*

When carbon dioxide is passed into water containing small particles of limestone in suspension, part of the carbon dioxide unites with the water to form carbonic acid. The carbonic acid so formed dissolves the limestone and the solution goes clear. (See Experiment 54, p. 88.) The solution of the lime-stone in carbonic acid solution is a chemical change resulting in the formation of a new substance called calcium bicarbonate.

$$\text{Calcium carbonate} + \left.\begin{array}{l}\text{hydrogen}\\\text{carbonate}\end{array}\right\} \text{form} \left\{\begin{array}{l}\text{calcium hydrogen}\\\text{carbonate,}\end{array}\right.$$
<div align="center">(carbonic acid)   (calcium bicarbonate)</div>

i.e. normal salt + acid form acid salt.
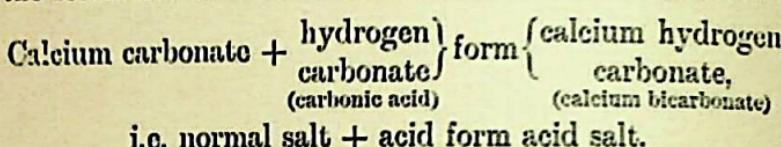
Compare this with the action of carbon dioxide upon a solution of washing-soda (sodium carbonate), by which baking-soda (sodium bicarbonate) is formed.

$$\text{Sodium carbonate} + \left.\begin{array}{l}\text{hydrogen}\\\text{carbonate}\end{array}\right\} \text{form} \left\{\begin{array}{l}\text{sodium hydrogen}\\\text{carbonate.}\end{array}\right.$$
<div align="center">(carbonic acid)   (sodium bicarbonate)</div>
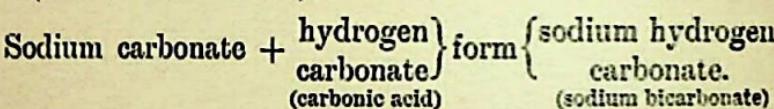
On boiling the water containing the calcium bicarbonate, the carbonic acid is decomposed into carbon dioxide and water. The carbon dioxide escapes as bubbles of gas, and the insoluble calcium carbonate is thrown out of solution (precipitated).

Or, it may be considered that the carbon dioxide, like other gases, is *less* soluble in hot water than it is in cold water. Hence, when the water is boiled the carbon dioxide is driven off, and the water alone is no longer able to hold the calcium carbonate in solution.

Similarly, it is the bicarbonate of magnesium which is in solution in spring-water and the magnesium carbonate which is precipitated on boiling.

River-water.—Exactly what solids are present in a certain spring will depend upon the kind of rock through which the water filters. At length the water will reach a layer of rock which is not porous, and will be forced to find an outlet on the hillside as a spring (fig. 60). As a river the water will receive other substances in solution or in suspension, and will probably

soon become so contaminated that it will be unfit for drinking purposes.

Sea-water.—The rivers empty their dissolved and suspended matters into the sea. It is the pure water only which is evaporated from the sea, so that the ocean must gradually get more and more salts in solution, and more and more insoluble substances deposited on its bed. Much of the calcium carbonate brought down by the rivers is removed from the sea by shell-fish in the formation of their shells.
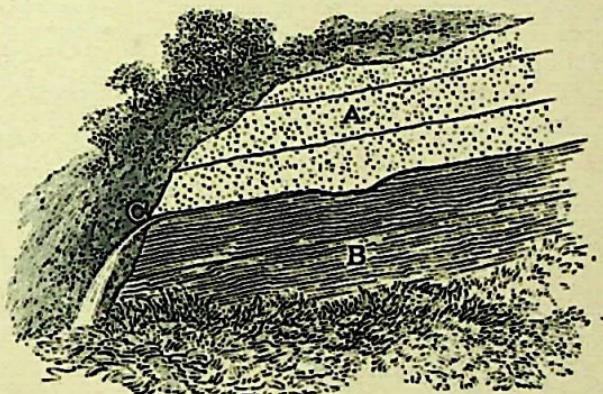
Fig. 60.—Formation of a Spring. Much of the rain which falls upon the sandstone (A) soaks into the rock until it reaches the bed of clay (B), through which it cannot pass. It then issues as a spring at C

The composition of the water of the British Channel is given below as a typical example of a sea-water:—

Water	964·745	grm.
Sodium chloride	27·059	,,
Magnesium chloride	3·666	,,
Magnesium sulphate	2·296	,,
Calcium sulphate	1·406	,,
Potassium chloride	·766	,,
Calcium carbonate	·033	,,
Magnesium bromide	·029	,,
	1000·000	,,

Mineral Waters.—Some spring-waters have an unusually

large amount of certain salts or gases dissolved in them. Such waters are called mineral waters. The term mineral water does not mean that the water contains a greater total weight of solids in solution than other waters contain, but that it contains a relatively larger amount of one or more substances.

Examples of mineral waters and their main constituents are given below:—

Mineral Water.	Chief Substance in Solution.
Chalybeate waters.	Iron carbonate.
Apollinaris and Seltzer waters.	Carbon dioxide.
Sulphur springs.	Sulphuretted hydrogen.
Saline waters.	Magnesium sulphate, and Magnesium chloride.

HARD AND SOFT WATERS

Experiment 67. — To compare the hardness of various samples of water.

A water is said to be " hard " when it fails to give an immediate lather with soap.

Use (a) tap-water, (b) distilled water, (c) boiled tap-water, (d) rain-water, (e) distilled water to which a few drops of calcium sulphate solution have been added.

A suitable soap solution for comparing the hardness of samples of water may be made by dissolving 1 grm. of Castile soap in 60 cu. cm. of water mixed with 30 cu. cm. of methylated spirit.

Obtain a burette and stand (fig. 61). Notice that the burette is graduated in cubic centimetres and tenths of a cubic centimetre. Remove the tap T, and rub it with a little vaseline to ensure that it will turn easily and yet be watertight. Replace the tap and fill the burette with the soap solution. Turn the tap and run out a little soap solution. This is done to replace the air in the tube below the tap by the solution.

(i) Read the level of the solution in the burette.   In doing so the eye must be on a level with the surface of the solution, and the reading taken at the *lowest* part of the meniscus. [Level = a cu. cm.]

Place 25 cu. cm. of tap-water in a bottle or small flask by means of a pipette.   Place the bottle under the burette and slightly turn the tap until 1 cu. cm. of the soap solution has run into the bottle.   Cork the bottle and shake it.   If a lather is produced, stand the bottle on the bench and see whether the lather remains for one minute.   If not, add another cubic centimetre of the soap solution to the water.   Shake again, and test the duration of the lather as before.

When enough soap solution has been added to produce, on shaking, a lather which will last one minute, the water has been softened by the soap.   Notice the pieces of solid which the water now contains.   They are the substance formed by the chemical action of the soap upon the substances in the water which made the water hard.

Read the level of the solution in the burette. [Level = b cu. cm.]   The amount of soap solution necessary to soften the water may be taken as a measure of the hardness of the water. The hardness of the tap-water will therefore be represented by the number $(b - a)$.

Fig. 61.—Burette and Stand

(ii) Repeat the experiment with the other samples of water to be tested.

To prepare the boiled water, the water should be measured before boiling (why?), then boiled in a small flask for a quarter of an hour and tested when cold.

Soap gives an *immediate* lather with rain-water and with distilled water.   These are therefore called "soft" waters.
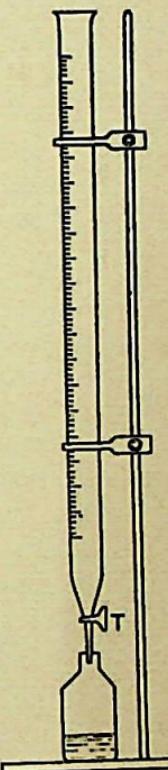
With spring-water (tap-water) soap does not give such a lather, and therefore does not begin to act as a cleansing agent until sufficient soap has been added to remove certain dissolved solids. Spring-water is therefore called a "hard" water.

After the spring-water has been boiled it is still hard, but not so hard as before. Boiling evidently removes *some* of the causes of the hardness.

It has already been stated that boiling removes the carbonates of lime and magnesium (p. 107). The inference is that part of the hardness of spring-water is due to the calcium bicarbonate and magnesium bicarbonate which are in solution in the water.

This part of the hardness, the part which can be removed by boiling, is called *temporary hardness.*

The hardness which remains after prolonged boiling, is due to the presence of calcium and magnesium sulphates or chlorides, and is called *permanent hardness.*

The permanent hardness is only comparatively permanent, for it can be removed by the addition of sodium carbonate to the water. The sodium carbonate acts upon the calcium sulphate and forms sodium sulphate and calcium carbonate. The calcium carbonate is insoluble, and the solution of sodium sulphate does not affect the soap, so that the hardness is removed.

Double Decomposition.—A reaction similar to the above is spoken of as a double decomposition. The calcium sulphate decomposes the sodium carbonate and the sodium carbonate decomposes the calcium sulphate. Double decomposition takes place to some extent whenever a solution of one salt, A, is added to a solution of another salt, B. The acid portion of A attaches itself to the basic portion of B, and the acid part of B unites with the basic part of A. Thus:—

A solution of sodium carbonate added to a solution of calcium sulphate } forms { sodium sulphate and calcium carbonate.

A solution of copper sulphate }
    added to   } forms { copper hydroxide
a solution of sodium hydroxide }   and
                                      sodium sulphate.

A solution of hydrogen sulphate }
      (sulphuric acid)   } forms { hydrogen chloride
    added to   }   (hydrochloric acid)
a solution of calcium chloride }   and
                                      calcium sulphate.

It will be seen from the examples just given that double decomposition is not limited to the solutions of salts, but also takes place between salts and hydroxides and between salts and acids.

In cases where one of the products of double decomposition is insoluble, this insoluble substance is deposited as quickly as it is formed, and double decomposition generally continues until almost all of one of the substances has been decomposed.

Clarke's Method of Softening Water.—A common method of removing temporary hardness is to add lime to the water. If sufficient lime is added the soluble bicarbonates of calcium and magnesium are changed into the insoluble carbonates (normal carbonates). In p. 108 it was stated that calcium carbonate in hard water may be considered to be held in solution by the carbonic acid in the water.

Anything, therefore, that removes the carbonic acid will cause the deposition of the calcium carbonate.

Boiling removes the carbonic acid by driving off the carbon dioxide. Lime removes the carbonic acid by neutralizing it, forming calcium carbonate (see p. 99).

Stalactites and Stalagmites.—It sometimes happens that water containing a large amount of calcium bicarbonate in solution drips through the roof of a cavern. As the drops of water hang from the roof some of the dissolved carbon dioxide escapes, and as a result a little limestone is deposited. Or the drop may fall on the floor of the cavern and deposit the limestone there. As this continues, a rod-like mass of lime-

stone grows downward from the roof (a stalactite) or upward from the floor (a stalagmite).

QUESTIONS ON CHAPTER XI

1. What is meant by "hard" and "soft" water? Describe what happens when you breathe into solutions of (a) sodium hydroxide, (b) calcium hydroxide. (C. L.)

2. A current of carbon dioxide is passed into lime-water. Describe the changes which take place. How will the hardness of the lime-water alter during the passage of the gas through the liquid? (C. L.)

3. It is stated that the air contains carbon dioxide. How could you prove this, and how do you account for the presence of that gas in air? What has the fact of its being there to do with the properties of many natural waters? (O. L.)

4. What reactions may take place on passing carbon dioxide through lime-water, and what may be the effects on the hardness of the water? (O. L.)

5. Explain what happens when water is softened by means of lime.

6. Distinguish between temporary and permanent hardness. To what is each due?

CHAPTER XII

EQUIVALENTS

In determining the composition of water by weight it was shown that 8 parts by weight of oxygen unite with 1 part by weight of hydrogen to form water (Chapter VII).

The number 8, which expresses the weight of oxygen which combines with 1 part by weight of hydrogen, *is called the equivalent weight (or equivalent) of oxygen.*

In Experiment 48 it was shown that magnesium oxide

consists of 60 per cent of magnesium and 40 per cent of oxygen.

∴ 60 grm. of magnesium combine with 40 grm. of oxygen,
or 12   ,,   ,,   ,,   8   ,,

The number 12 is called the equivalent of magnesium because it expresses the number of grammes of magnesium which will combine with 8 grm. of oxygen.

But 8 grm. of oxygen have been shown to be equivalent to 1 grm. of hydrogen.

Hence 12 grm. of magnesium are equivalent to 1 grm. of hydrogen.

The equivalent weight of an element is a number representing the weight of that element which combines with (or displaces) 1 part by weight of hydrogen or 8 parts by weight of oxygen.

It is here assumed that the weight of an element which will combine with 8 parts by weight of oxygen is the same weight as is required to displace 1 part by weight of hydrogen.

Let us test this assumption.

Experiment 68.—To find the equivalent of magnesium by the displacement of hydrogen from an acid.

See also Experiment 71.

The apparatus used in Experiment 61 (fig. 56 (ii)) may be employed. It is advisable, however, to use concentrated sulphuric acid in the small test-tube, and to replace the calcium chloride in the drying-tube by glass-wool soaked in concentrated sulphuric acid. Since hydrogen is such a very light gas the experiment must be performed with the greatest care in order to get even a fairly accurate result.

Weigh about ·5 grm. of magnesium wire. (Weight = a grm.) Remove the drying-tube D (fig. 56 (ii)) from the apparatus. Empty it and then nearly fill it with glass-wool. Pour concentrated sulphuric acid on the glass-wool, and allow the excess of acid to drain into a beaker.

Place about 6 cu. cm. of concentrated sulphuric acid in A and 10 cu. cm. of distilled water in L (fig. 56). Also place the weighed magnesium wire in L. Replace the drying-tube and insert the plug P. (Why?) Weigh the apparatus as accurately as possible. (Weight = b grm.)

Remove the plug P and tilt the apparatus to allow a *little* of the acid in A to reach the magnesium. [If the acid is added in large quantities the flask will get warm. This will cause water vapour to come off so rapidly that some of it will escape into the air.] If the flask *should* get warm, place the lower part of it in a dish of cold water. The magnesium acts upon the acid, forming magnesium sulphate and setting free hydrogen. When the reaction ceases add another drop of acid from A to the magnesium. Continue the addition of the acid from A until the magnesium is completely dissolved. Attach a piece of glass tubing to R, and suck out the hydrogen left in the flask. Replace the plug P and weigh the apparatus very accurately. (Weight = c grm.)

Calculate the equivalent of magnesium as in the example below:—

Weight of magnesium $= \cdot5$ grm. (a).
    ,,   apparatus before the reaction $= 70\cdot535$,, (b).
    ,,   ,,   after   ,, $= 70\cdot490$,, (c).
    ,,   hydrogen set free $= \cdot045$,, ($b - c$).
Then, $\cdot045$ grm. of hydrogen is set free by $\cdot5$ grm. of magnesium.
$\therefore$ 1   ,,   ,,   ,, $11\cdot1$,,   ,,
      i.e. the equivalent of magnesium $= 11\cdot1$

Very careful experiments similar to the above have shown that the equivalent of magnesium as found by the displacement of hydrogen from an acid is 12. The equivalent of magnesium as found by determining the weight of magnesium which will unite with 8 grm. of oxygen is 12.

In the case of magnesium, therefore, we are justified in assuming that the weight of magnesium which will displace 1 grm. of hydrogen is also the weight of magnesium which will combine with 8 grm. of oxygen.

The same rule has been shown to be true for the other elements.

Experiment 69.—To find the equivalent of an element by the formation of its oxide.

Weigh a clean, dry crucible and lid. In it place about ·5 grm. of copper, and weigh again. Tilt the lid slightly, and add one drop of concentrated nitric acid by means of a pipette. When the reaction ceases add another drop of nitric acid. The nitric acid acts upon the copper, forming copper nitrate and setting free oxides of nitrogen (red fumes). Place the crucible on a piece of asbestos and warm it gently by means of a small flame held some distance below the crucible. Add a few more drops of nitric acid, and when the liquid has evaporated, gradually increase the size of the flame. Finally, heat the crucible as strongly as possible for ten minutes. This will decompose the copper nitrate into copper oxide and oxides of nitrogen. See that there is no blue copper nitrate undecomposed on the lid of the crucible. Allow the crucible and lid to cool, then weigh them.

Add two more drops of nitric acid, and heat again very gradually until the liquid has evaporated, and then heat very strongly. Cool and weigh the crucible and its contents. Repeat the addition of nitric acid and the subsequent operations until the weight remains constant. Calculate the equivalent of copper, as in the following example:—

Example—

Weight of crucible			$=$	$9·21$ grm.
,,	,,	$+$ copper	$=$	$9·90$,,
,,	,,	$+$ copper oxide	$=$	$10·07$,,
,,	copper		$=$	$·69$,,
,,	oxygen		$=$	$·17$,,

·17 grm. of oxygen unites with ·69 grm. of copper.

$\therefore$ 8 ,, ,, ,, $\dfrac{·69 \times 8}{·17} = 32·4$ grm. of copper.

i.e. the equivalent of copper is $32·4$.

The equivalent of some metals may be found by displacing the metal from one of its salts by means of a metal whose equivalent is known already.

Thus zinc will displace copper from copper sulphate, forming copper and zinc sulphate.

Magnesium will displace silver from silver nitrate, forming silver and magnesium nitrate.

Experiment 70.—To find the equivalent of copper by the displacement of the metal from copper sulphate by means of zinc.

Weigh a clean, dry evaporating-dish. Place in it about ·5 grm. of zinc-foil which has had the oxide scraped off. Weigh again to obtain the weight of the zinc. Half fill the dish with pure copper sulphate solution. Notice that the zinc dissolves and reddish-brown copper makes its appearance. The action may be hastened by warming the solution. If the blue colour is entirely destroyed, more copper sulphate solution must be added.

Finally, when no zinc remains undissolved, allow the copper to settle, and decant the liquid. Be careful not to allow any of the copper to escape. Add water to the contents of the evaporating-dish, and stir by means of a stirring-rod to wash the copper. Decant again. Continue the washing several times with water, and finally with methylated spirit. The spirit will prevent oxidation of the copper while it is being dried. Dry the evaporating-dish and the copper in it in an air-oven or on a steam-bath. Do not make the copper hot or it will oxidize. When they are quite dry, weigh the dish and its contents. Calculate the equivalent of copper as below, given that the equivalent of zinc is $32\frac{1}{2}$.

Example—

Weight of evaporating-dish				= 44·050 grm.
,,	,,	,,	+ zinc =	44·675 ,,
,,	,,	,,	+ copper =	44·655 ,,
,,	copper		=	·605 ,,
,,	zinc		=	·625 ,,

Hence ·625 grm. of zinc displaces ·605 grm. of copper.

∴ $32\frac{1}{2}$,, displace $\dfrac{32\cdot5 \times \cdot605}{\cdot625} = 31\cdot4$ grm. of copper.

i.e. the equivalent of copper = 31·4.

Experiment 71.—To find the volume of hydrogen set free from an acid by the equivalent weight of a metal.

Use magnesium and either sulphuric acid or hydrochloric acid.

Fit up the apparatus shown in fig. 62. w is a " Winchester quart" or other large bottle having a capacity of about 2 litres. It should be nearly full of water. F is a small flask, say
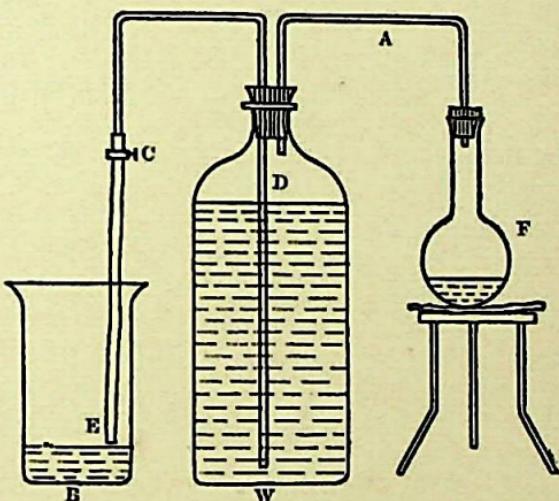
Fig. 62.—Measurement of the Volume of Gas set free during a Reaction

100 cu. cm. C is a clip. All the tubes are of glass except C E, which is of rubber. The stoppers are of rubber, because the apparatus when fitted up must be air-tight. Notice that the end of the glass tube A is *above* the level of the water in W, also observe that the tube D reaches nearly to the bottom of W.

Test the apparatus to see that it is air-tight. To do so, open the clip and blow a few bubbles of air through E into W. The water will rise in D because of the increase in pressure in W. Tighten the clip. If the height of the water in D remains constant there is no leakage, and the experiment may be proceeded with. If the height of the water in D gradually decreases, the tubes and stoppers must be fitted more securely.

Weigh carefully about ·25 grm. of clean magnesium wire. (Weight = w grm.) Open the clip C and suck water from W into the tube E. When D and E are full of water close the clip. Place the empty beaker B (capacity 500 cu. cm.) under the tube E. Place about 10 cu. cm. of concentrated hydrochloric acid, diluted with 20 cu. cm. of water, into F. Roll the weighed magnesium wire into a ball and wedge it in the neck of the flask, so that it will *not* slip into the acid. Insert the stopper of F tightly. The glass delivery-tube from F should then be pushed through the cork on the magnesium wire to force it into the acid.

Open the clip, and the hydrogen set free in F will displace an equal volume of water from W into B. Wait ten minutes, to allow the gas to reach the temperature of the room, then level the water surfaces in B and W by raising B. The gas in W is then under atmospheric pressure.

Read the barometer so as to be able to state the pressure. [Pressure = p cm.]

Read also the laboratory temperature. [Temperature = $t°$ C.]

Measure the volume of water collected in B. [Volume = v cu. cm.] This represents the volume of moist hydrogen at p cm. pressure and $t°$ C., set free by w grm. of magnesium.

Calculate the volume this hydrogen would occupy if it were dry hydrogen under a pressure of 76 cm. and at a temperature of 0° C., as in the example below.

Example—

Temperature	= 16° C. (t).
Barometer reading	= 75 cm. (p).
Weight of magnesium used	= ·43 grm. (w).
Volume of hydrogen collected	= 420 cu. cm. (v).

We will first reduce the volume of hydrogen collected to normal temperature and pressure. To do so we will make use of the equation—

$$\frac{p_1 v_1}{p_2 v_2} = \frac{1 + \dfrac{t_1}{273}}{1 + \dfrac{t_2}{273}}$$

obtained by combining Boyle's Law $(p \cdot v = k)$* and Charles' Law

$$\left(\frac{p_1}{p_2} = \frac{1 + a t_1}{1 + a t_2}\right)^*$$

where p = pressure,
v = volume,
t = temperature in C.°,
k is a constant, and
$a = \frac{1}{273}$.

Substituting the values in the first equation we obtain—

$$\frac{76 \cdot v_1}{75 \times 420} = \frac{1 + \dfrac{0}{273}}{1 + \dfrac{16}{273}}$$

$$\frac{76 \cdot v_1}{31500} = \frac{273}{289}$$

$$v_1 = \begin{cases} 391 \text{ cu. cm. of hydrogen at } 0° \text{ C.} \\ \text{and 76 cm.} \end{cases}$$

Weight of 1000 cu. cm. of hydrogen = ·09 grm.
  „   „ 391   „   „   „ = $\frac{·09 \times 391}{1000}$ = ·0352 grm.

·0352 grm. of hydrogen is set free by ·43 grm. of magnesium.

∴ 1 „   „   „ $\frac{·43}{·0352}$ = 12·2 grm. of magnesium,

i.e. equivalent of magnesium = 12·2.

Methods of Determining Equivalent Weights. — The methods of determining the equivalent weight of an element which have been considered in this chapter are summarized below.

(i) By direct combination with hydrogen, as in the case of oxygen.

(ii) By direct combination with oxygen. This method is applicable in a very large number of cases, since most elements will combine with oxygen. In the case of the metals it is usually most convenient to form the nitrate first and then ignite it to obtain the oxide.

(iii) By displacement of hydrogen from an acid.

(iv) By displacement of a metal whose equivalent is known from a solution of one of its salts.

* See pp. 96 and 232 in *A Course of Physics*, published by Messrs. Blackie & Son.

QUESTIONS ON CHAPTER XII

1. What is meant by the equivalent weight of an element? 0·72 grm. of metal displaces 244 cu. cm. of hydrogen at 0° C. and 760 mm. pressure. Calculate the equivalent weight of the metal. (C. L.)

[1 litre of hydrogen at 0° C. and 760 mm. pressure weighs ·09 grm.]

2. What do you understand by the equivalent weight of an element? Describe carefully how you would determine the equivalent weight *either* of copper *or* of magnesium. (C. L.)

3. Describe a method by which you would determine the equivalent weight of zinc.

CHAPTER XIII

HYDROCHLORIC ACID AND CHLORINE

Experiment 72.—To find the effect of sulphuric acid upon common salt.

Place a few grammes of common salt in a test-tube, and add to it a little concentrated sulphuric acid. Notice the effervescence which occurs. Cautiously smell the gas which is evolved. Observe that the gas fumes as it reaches the air, and that the fumes become denser when breathed upon, or when in contact with a glass rod previously wetted with ammonium hydroxide. Can you identify the gas by its smell?

Hold a wet piece of blue litmus-paper in the mouth of the test-tube. Is the gas an acid gas?

As soon as the effervescence ceases place a cork in the open end of the test-tube. Invert the test-tube in a beaker of water and remove the cork. Is the gas soluble in water?

The gas obtained by the action of sulphuric acid upon common salt (sodium chloride) is called hydrochloric acid.

Try the effect of concentrated sulphuric acid upon ammonium chloride, potassium chloride, and calcium chloride in

turn.   Do other chlorides yield hydrochloric acid on treatment with sulphuric acid?

Experiment 73.—To prepare hydrochloric acid and to examine its properties.

(i) Fit up the apparatus shown in fig. 63. See that the bottom of the thistle funnel T almost touches the bottom of the flask.   Notice also that the end of the delivery-tube D is near the bottom of the gas-jar or bottle B.   The gas-jar must be quite dry inside.   Why?

Place about 30 grm. of common salt in the flask F. Dilute some sulphuric acid with its own volume of water.   Pour enough of the acid into F to cover the lower end of the thistle funnel.   Why must the end of the thistle funnel be below the acid?

Warm the flask F gently, and collect the hydrochloric acid by downward displacement. When the reaction in the flask slackens add a little more acid.

Fig. 63.—Preparation of Hydrochloric Acid Gas

When the gas-jar is full of hydrochloric acid gas, the overflowing gas will be seen to form white fumes as it reaches the air outside. Remove the jar when it is full of the gas, cover it with a greased plate, and proceed to collect another jar full of the gas.   In this way collect four jars full of hydrochloric acid gas.

(ii) Examine the gas according to the usual scheme (p. 46). Then shake up a few cubic centimetres of concentrated ammonium hydroxide in a gas-jar covered with a greased plate.   This will fill the gas-jar with ammonia gas.   Place a jar of hydrochloric acid gas mouth to mouth with the jar of ammonia gas (fig. 64). Let the heavier hydrochloric acid be above the lighter ammonia.   Remove the greased plate to allow the gases to mingle.   What happens?
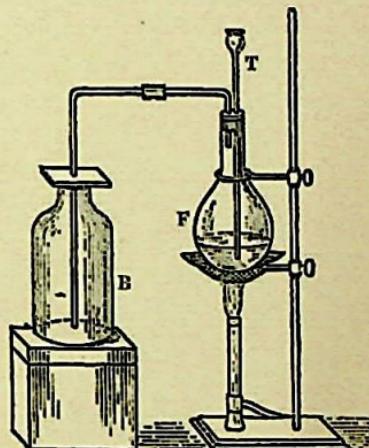
Ammonia is a base, hydrochloric acid is an acid, and the white powder which settles down in the gas-jars is the salt ammonium chloride formed by the neutralization of the acid by the base.

$$\begin{matrix}\text{Ammonium}\\\text{hydroxide}\end{matrix} + \begin{matrix}\text{hydrogen chloride}\\\text{(hydrochloric acid)}\end{matrix} = \begin{matrix}\text{ammonium}\\\text{chloride}\end{matrix} + \text{water.}$$
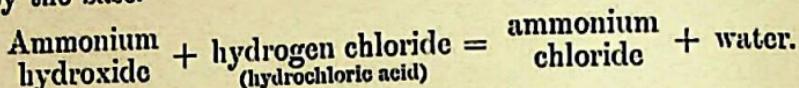
Experiment 74.—To make a strong aqueous solution of hydrochloric acid gas.

Fig. 64. — Formation of Ammonium Chloride

The apparatus used for generating hydrochloric acid gas may be used. If the end of the delivery-tube were simply placed in water, as soon as the gas ceased to come off from F (fig. 63) the water would dissolve the gas in the delivery-tube and rush over into F. To prevent this, a funnel should be attached to the end of the delivery-tube by means of rubber tubing. A little water is then placed in a beaker, and the funnel arranged so that it just dips into the water (fig. 65). Pass hydrochloric acid gas through the water until a strong solution of the gas has been obtained. Pour a little of the solution of hydrochloric acid into a test-tube. Add one or two drops of silver nitrate solution. Notice the white precipitate of silver chloride which forms. Add ammonium hydroxide to the contents of the test-tube until the silver chloride dissolves.

Fig. 65.—Preparation of an Aqueous Solution of Hydrochloric Acid Gas

$$\begin{matrix}\text{Hydrochloric}\\\text{acid}\end{matrix} + \begin{matrix}\text{silver}\\\text{nitrate}\end{matrix} \Big\} \text{ form } \Big\{ \begin{matrix}\text{nitric}\\\text{acid}\end{matrix} + \begin{matrix}\text{silver}\\\text{chloride.}\end{matrix}$$
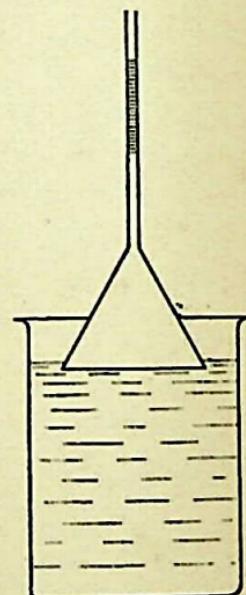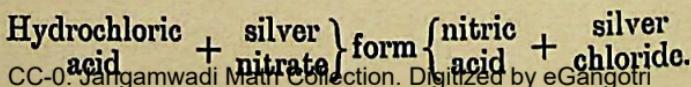
This test is often employed as a means of identifying hydro-chloric acid.

Also find the effect of the solution of hydrochloric acid gas upon the metals zinc, iron, magnesium, and copper. Compare the results with those obtained in Experiment 49.

Preparation.—Hydrochloric acid is prepared by the action of concentrated sulphuric acid upon a chloride. Sodium chloride is generally used.

Hydrogen sulphate + sodium chloride } form { hydrogen chloride + sodium sulphate.
(sulphuric acid)   (common salt)   (hydrochloric acid)
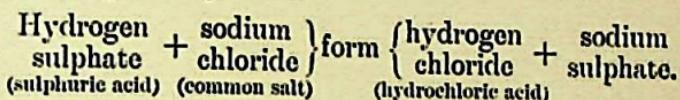
Notice the double decomposition.

With less salt and the lower temperature used in the laboratory the reaction is:—

Sulphuric acid + sodium chloride } form { hydrochloric acid + sodium hydrogen sulphate.
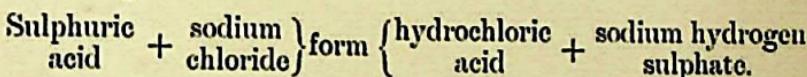
Hydrochloric acid is made in large quantities as a by-product in the manufacture of washing-soda (sodium carbonate) by the Leblanc process (p. 257). The yellow colour of the commercial acid is due to the presence of impurities, chiefly iron chloride.

Properties.—Hydrochloric acid is a colourless gas with a strong characteristic smell. When inhaled it gives a choking sensation. It fumes in moist air. This fuming is due to the gas dissolving in the particles of water vapour present in the air. Hydrochloric acid will not burn, neither will it support combustion. It is very soluble in water, and about $1\frac{1}{4}$ times as heavy as air. Hence it may be collected over mercury, or by downward displacement of air, but *not* over water.

The great solubility of the gas may be strikingly shown by collecting a large round-bottomed flask full of the gas. The flask is fitted with a stopper carrying a glass tube. If the end of the glass tube is placed in a jar of water, the water will gradually rise up the glass tube, and ultimately form a fountain inside the flask.

The experiment may be hastened by wetting the inside of the glass tube before inserting it in the flask. If the water used be coloured with blue litmus solution, the acid nature of the gas is also apparent (fig. 78).

Composition of Hydrochloric Acid.—We have previously seen that when hydrochloric acid is acted upon by various metals, hydrogen is evolved. (See p. 83.) This might at first sight seem to prove that hydrochloric acid contains hydrogen. It does not prove this. The hydrochloric acid then used was really a solution of hydrochloric acid gas in *water*. The hydrogen *may* therefore have come from the water.

If it is possible to obtain hydrogen from the dry, gaseous hydrochloric acid it will prove that the hydrogen does not come from the water.

Experiment 75.—**To show that hydrogen is evolved when dry hydrochloric acid gas is acted upon by a metal, and to examine the residue.**

Fig. 66.—Action of Gaseous Hydrochloric Acid upon a metal. Preparation of the dry gas

Use sodium as the metal.

(i) Fit up the apparatus shown in figs. 66 and 67. The gas is generated in the flask F exactly as in Experiment 73. The bottle B contains concentrated sulphuric acid to dry the gas. The combustion-tube E (fig. 67) should be joined to D (fig. 66) by means of a rubber tube, and supported horizontally. A long thin slice of sodium —about $\frac{1}{4}$ grm.—should be placed in the combustion-tube. A jet at which to light the escaping hydrogen should be fitted on the open end of the

combustion-tube (J, fig. 67). Pass a current of hydrochloric acid gas from F over the sodium. When the hydrochloric acid has displaced the air from the apparatus, heat the sodium by means of a Bunsen burner. To prevent an explosion, satisfy yourself (see p. 59) that the issuing gas is unmixed with air. Then light the gas as it issues from the jet. Apply any other tests which you know to the gas to prove that it is hydrogen.

(ii) To examine the substance formed when sodium acts upon hydrochloric acid.
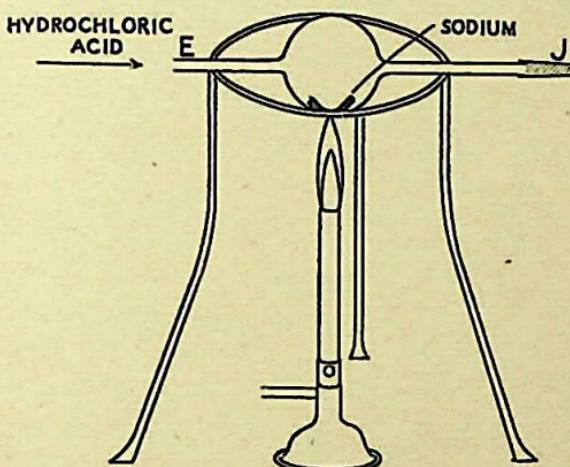
Fig. 67.—Action of Gaseous Hydrochloric Acid upon a Metal

Remove the remains of the sodium from the combustion-tube. Scrape off a little of the white powder with which it is coated. Dissolve it in a few drops of water and allow the solid to crystallize out in a watch-glass. Examine the crystals by means of a lens or microscope. Compare their shape with that of crystals of common salt. The substance *is* common salt. How could you prove it to be common salt if you had a larger quantity of it? See Experiment 72.

Evidently, then, hydrochloric acid contains hydrogen replaceable by a metal—it also forms salts called chlorides when neutralized by bases—and so has rightly been termed an acid. When sodium neutralizes hydrochloric acid, hydrogen is set free and sodium chloride (common salt) is formed. The next

aim must be to obtain the other element or elements with which the hydrogen is combined to form hydrochloric acid.

The effect of heat upon hydrochloric acid or upon common salt—which must also contain the other element (or elements) —fails to liberate the element (or elements).

Therefore we will try to remove the *hydrogen* from hydro-chloric acid, so as to leave the other element (or elements) behind. This may be effected by oxidizing the hydrogen to water. We will remove the hydrogen in this way, using manganese dioxide as the oxidizing agent.

Experiment 76.—To remove hydrogen from hydro-chloric acid by means of manganese dioxide.

(i) Place a little salt and an equal quantity of manganese dioxide in a test-tube. Add a little concentrated sulphuric acid, and warm the mixture. The gas evolved is poisonous, and should be smelled with caution. Notice the greenish-yellow colour of the gas. This is the other element combined with hydrogen to form hydrochloric acid. It is called *chlorine*.

(ii) Warm a mixture of 1 cu. cm. of water and 1 cu. cm. of concentrated hydrochloric acid and a little manganese dioxide in a test-tube. Observe that in this case also chlorine is given off.

Evidently either the gas chlorine is present in the hydro-chloric acid, and also in common salt, or else it comes from the manganese dioxide.

Fortunately we are not limited to manganese dioxide as a means of oxidizing the hydrogen of hydrochloric acid and leaving the chlorine. Many oxidizing agents, such as red lead, potassium bichromate, and potassium chlorate, have the same effect. Red lead, for example, added to concentrated hydro-chloric acid yields chlorine on heating.

Now red lead contains no chlorine, for it may be formed by heating lead in air or oxygen. This points to the fact that chlorine is the other element (or one of the other elements) in hydrochloric acid.

Experiment 77.—To electrolyse hydrochloric acid.

A commonly accepted, but very unsatisfactory, method of analysing hydrochloric acid is by means of electrolysis.

The voltameter shown in fig. 68 is used.

Since platinum is attacked by chlorine, electrodes E E of hard-gas carbon are used. The electrodes are connected to an electric battery, and a current of electricity passed through the concentrated hydrochloric acid with which the voltameter is filled. At first hydrogen seems to be given off much more freely than chlorine. This is due to the fact that chlorine is soluble in hydrochloric acid. When the acid has become saturated with chlorine, the two gases— hydrogen and chlorine—should collect at equal rates. Quantitatively the experiment is very unsatisfactory. Qualitatively it shows that hydrochloric acid consists of hydrogen and chlorine if it is assumed that the water present takes no part in the reaction.

This completes our *analysis* of hydrochloric acid. It will be seen, when the synthesis of the acid is considered, that hydrochloric acid contains only hydrogen and chlorine, and that they are combined in equal volumes.

Distribution.—Hydrochloric acid occurs naturally in the gases evolved from volcanoes during eruption. The salts of hydrochloric acid (chlorides) are very abundant. The commonest chloride is common salt. Rock salt is found in Cheshire and Worcester (England), round Stassfurt in Saxony (Germany), Wielicza (Austria), Cardona (Spain), many parts of the United States, Punjaub (India), and many other places.
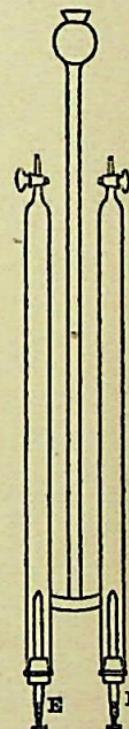
Fig. 68. — Electrolysis of Hydrochloric Acid (solution)

CHLORINE

Experiment 78.—To prepare chlorine and to examine its properties.

This experiment should be conducted in a fume-chamber or out-of-doors.

Use the same apparatus as in Experiment 72, fig. 63. A gas-jar is preferable to the bottle shown in the figure.

A mixture of equal weights of hydrochloric acid and manganese dioxide are placed in the flask and made into a paste. The delivery-tube is then fitted and the mixture heated. Chlorine is given off and is collected by downward displacement, since it is rather soluble in water and is a heavy gas. Collect several jars full of the gas and examine its properties according to the usual scheme (p. 46). Also perform the following experiments with the gas to illustrate the readiness and vigour with which it combines with hydrogen or metals.

Fig. 69.—Formation of Hydrochloric Acid Gas by burning Hydrogen in Chlorine

(i) Fit a test-tube with a cork, and a delivery-tube as in fig. 69.

In the test-tube place some zinc and hydrochloric acid in order to generate hydrogen. *Satisfy yourself that all the air has been expelled from the apparatus by the hydrogen* (see p. 59). Then light the hydrogen as it issues from the delivery-tube. Lower the hydrogen flame into a jar of chlorine.

Notice that the hydrogen burns in chlorine with a smokeless flame. When the hydrogen has been burning for a short time, remove the flame. Test the solubility and acidity of the gas
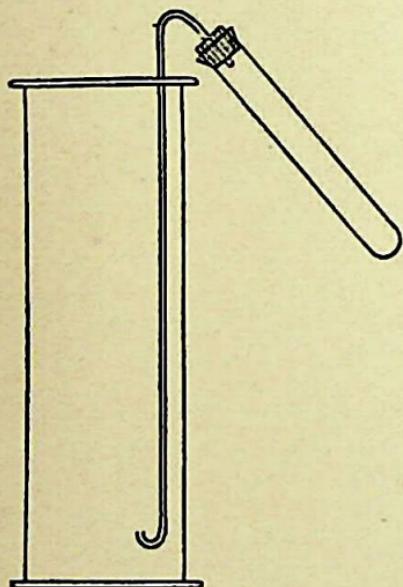
left in the gas-jar. Show by testing the solution with silver nitrate, as on p. 124, that *the gas produced when hydrogen burns in chlorine is hydrochloric acid.*

(ii) Pour a few drops of warm turpentine (a compound of hydrogen and carbon) upon a filter-paper. Drop the paper into a jar of chlorine. Notice that the turpentine inflames, and dense clouds of soot are formed.

The hydrogen of the turpentine combines with the chlorine and forms hydrochloric acid. The carbon of the turpentine is deposited as soot. *Chlorine has no action upon carbon.*

(iii) Drop a pinch of powdered *antimony* into a jar of chlorine. Notice that the antimony takes fire in the gas, and a white powder is formed.

(iv) Repeat (iii), using separately *phosphorus* and thin *copper-foil* (Dutch metal). Notice that both take fire in the gas.

(v) Write in ink on a piece of paper on which is some printing. Wet the paper and drop it into a jar of chlorine. Also drop in a leaf of a coloured flower.

After a while it will be noticed that the colour of the leaf and of the writing-ink has been destroyed (bleached). The printer's ink, however, will be found to be unaffected.

Shake up a jar of chlorine with a little water. Add a little of the solution of chlorine so formed to (*a*) a solution of potassium bromide, (*b*) a solution of potassium iodide.

Notice that in the case of the potassium bromide a yellowish solution is produced.

The colour is due to the liquid *bromine* displaced from the potassium bromide by the chlorine. In the case of potassium iodide the chlorine displaces the *iodine*, which colours the liquid brown. If now a little starch-paste be added to the solution, the *iodine will colour the starch blue.*

Properties.—Chlorine is a greenish-yellow gas with a characteristic irritating smell. It attacks the membrane of the mouth and throat. It is somewhat soluble in water. The solution gradually decomposes, because the hydrogen of the water slowly unites with the chlorine, forming hydrochloric acid, and the oxygen is set free from the water.

Chlorine will not burn, but allows many elements to burn in it.

Sodium will burn in chlorine and form sodium chloride.

Potassium	„	„	„	potassium „
Magnesium	„	„	„	magnesium „
Phosphorus	„	„	„	phosphorus „
Antimony	„	·,	„	antimony „
Hydrogen	„	„	„	hydrogen „
				(hydrochloric acid).

The affinity of chlorine for metals is made use of in one process for extracting gold from its ore. The ore after roasting is exposed to the action of chlorine. Gold chloride is formed, and this is dissolved in water.

Hydrogen and chlorine, if mixed, will unite to form hydrochloric acid, (i) slowly in diffused daylight but not at all in darkness, (ii) with explosive violence in bright sunlight or if a flame be applied to the mixture.

The great affinity of chlorine for hydrogen causes chlorine to be a powerful *oxidizing* and *bleaching* agent. Chlorine only bleaches when water is present. The chlorine unites with the hydrogen of the water, and the oxygen set free attacks the colouring matter and oxidizes it into a colourless compound.

Ordinary oxygen will not bleach. Evidently the oxygen *at the instant it is set free* from the water has properties which it does not possess later. Such oxygen is spoken of as *nascent oxygen.*

Chlorine is sold for bleaching and disinfecting purposes as *bleaching-powder.* Bleaching-powder is a compound of lime and chlorine. It is made by exposing lime to the action of chlorine until the lime has absorbed as much chlorine as possible. When used for bleaching purposes the chlorine is set free by means of very dilute acid.

Composition of Hydrochloric Acid. (*Synthesis.*)

Experiment 79.—Take a tube similar to the one shown

in fig. 70. The stopcock T and the stoppers S S should be greased with vaseline and the tube thoroughly dried.

Close the stopcock and fill the shorter limb with pure dry chlorine. Insert the stopper. [The chlorine may be generated, as usual, from manganese dioxide and hydrochloric acid. It should then be passed through a bottle of water to remove any hydrochloric acid and then through a bottle of sulphuric acid to dry the gas.]

Then fill the long limb of the tube with pure dry hydrogen. Insert the stopper.

Open the stopcock, and leave the tube in a dark cupboard for a week to allow the gases to mix. (Why is the tube kept in the dark?)
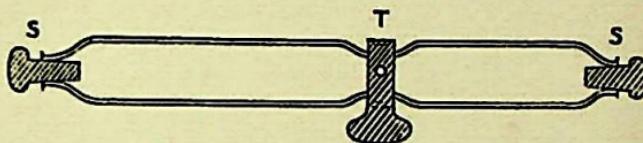
Fig. 70.—Composition of Hydrochloric Acid Gas

When the gases have mixed, expose the tube to diffused daylight (why not direct sunlight?) until the green colour of the chlorine has disappeared. Then open the stopper under mercury, and notice that no gas escapes, neither does any mercury enter the tube. This indicates that *when hydrogen and chlorine unite to form hydrochloric acid, they do so without change of volume.*

Introduce a little water into the tube, to absorb the hydrochloric acid formed. Notice that this causes the mercury to rise up the tube. Measure the volume of gas left in the tube. (a cu. cm.) Show that it is hydrogen. Find the capacity of each limb of the tube. (b cu. cm. of hydrogen and c cu. cm. of chlorine.)

Then ($b - a$) cu. cm. of hydrogen combines with c cu. cm. of chlorine to form ($b - a + c$) cu. cm. of hydrochloric acid.

It will be found that ($b - a$) = c.

This shows that *1 volume of hydrogen unites with 1 volume of chlorine to form 2 volumes of hydrochloric acid.*

Composition of Hydrochloric Acid. (*Analysis.*)

The fact that hydrochloric acid contains half its volume of hydrogen may also be shown by the following experiment.

Experiment 80.—The long tube employed in Experiment 30 (fig. 27) may be used. It should be dried and filled with hydrochloric acid collected over mercury. When full of the gas, a few cubic centimetres of sodium amalgam (a solution of sodium in mercury) are added and a rubber stopper fitted. The sodium will unite with the chlorine in the hydrochloric acid and liberate the hydrogen. The mercury combined with sodium serves to make the action of the sodium upon the hydrochloric acid less vigorous.

If now the stopper be removed from the tube while the end is under water, the water will rise and about half fill the tube. The volume of the residual gas should be measured at atmospheric pressure and the capacity of the tube found. It will be seen that the *volume of gas left is exactly half the volume of the hydrochloric acid used.* The residual gas may be shown to be hydrogen by the fact that it will burn and form water.

Distribution.—Chlorine is not found free in nature. Combined with metals, as chlorides, it is very abundant.

QUESTIONS ON CHAPTER XIII

1. How is hydrochloric acid prepared? Why is it called an acid? How does hydrochloric acid react chemically with (*a*) ammonia, (*b*) sodium hydroxide, (*c*) sodium carbonate, (*d*) iron? (C. L.)

2. How is chlorine prepared? Describe experiments you would perform with this gas to illustrate its character. (C. L.)

3. What are the chemical reactions between a solution of hydrochloric acid and (*a*) manganese dioxide, (*b*) calcium oxide, (*c*) ammonia gas, (*d*) mercuric oxide, (*e*) sodium?

4. How may chlorine be obtained from common salt? State what happens when chlorine is passed into aqueous solutions of (*a*) sulphur dioxide, (*b*) caustic potash. (C. L.)

5. What happens when a mixture of sodium chloride with moderately concentrated sulphuric acid is gently heated? Describe, with a sketch, how you would collect the gaseous products of the reaction, and say what properties you would expect it to have. (O. L.)

6. Give as many methods as you can for the preparation of chlorine. What is the action of this gas upon (a) metallic sodium, (b) sulphuretted hydrogen, (c) a piece of dry red cloth? (O. L.)

7. Give a short account of the methods used in preparing the following substances from common salt (sodium chloride):— (a) hydrochloric acid gas, (b) chlorine.

What is the action of chlorine on hydrogen, on iron, and on slaked lime? (O. L.)

8. What are the chief sources from which chlorine is obtained? Describe fully one way in which it is prepared and collected, its chief chemical properties and practical uses. (O. L.)

9. State the experiments you would make to distinguish between hydrochloric acid gas and a mixture of equal volumes of hydrogen and oxygen. (C. L.)

CHAPTER XIV

NITROGEN AND ITS COMPOUNDS—NITROGEN

Experiment 81.—To prepare nitrogen from the air and to examine its properties.

(i) Fill the flask D and the tube E (fig. 71) with water. Close the clip C. Connect up the remainder of the apparatus as shown in the diagram.

A is a flask containing caustic soda. Notice that the inlet-tube dips well below the surface of the caustic soda.

B is a Ramsay burner supporting a combustion-tube which contains a roll of copper gauze. This burner provides a long

flat non-luminous flame, any part of which may be cut off by means of sliding pieces of metal.

F F are pieces of asbestos card to prevent the charring of the rubber stoppers which close the ends of the combustion-tube.

Light the burner and gradually make the combustion-tube red-hot. Open the clip C slightly, so that the air bubbles very slowly through A.

Since E is full of water, it forms a siphon,[1] and the water in D will pass over into the beaker as soon as the clip is opened. This will cause D to act as an aspirator. Air will
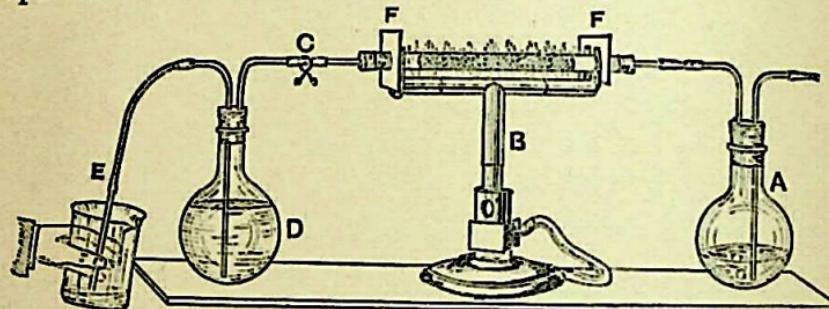
Fig. 71.—Preparation of Nitrogen from Air

leave A after bubbling through the caustic soda, which deprives it of its carbon dioxide. It will then pass over the heated copper gauze in the combustion-tube, and the copper will deprive the air of its oxygen.

When D is three-quarters full of nitrogen close the clip to stop the flow of air. Turn out the burner, and—

(ii) *examine the nitrogen in* D according to the usual scheme (p. 46).

The gas may, if desired, be transferred to a test-tube or gas-jar as follows: Arrange a delivery-tube, gas-jar, bee-hive shelf, and pneumatic trough as in fig. 32. Connect the delivery-tube to the flask containing the nitrogen by means of the rubber tube carrying the clip C (fig. 71). Open the clip. Raise the beaker until the level of the water in it is above the level of the water in D. Water will then siphon from the

[1] See p. 91 of *A Course in Physics*, published by Messrs. Blackie & Son.

beaker to D. This will drive some of the nitrogen from D into the collecting-vessel.

What substance is formed in A during the experiment? What compound covers the copper gauze at the close of the experiment? How do you propose to restore the copper gauze to its original condition for future use?

The method adopted in Experiment 81 for preparing nitrogen has been used by Dumas to determine the composition of the air by weight.

He collected the nitrogen in a very large flask (15 litres) provided with a stopcock. The air had previously been pumped out of this flask. The weight of this empty flask was known. The weight of the copper and combustion-tube were also determined.

The globe and the combustion-tube were again weighed at the close of the experiment.

The nitrogen remaining in the connecting-tubes was also weighed and added to the weight of nitrogen in the flask.

The increase in weight of the flask gives the weight of nitrogen. The increase in weight of the copper gives the weight of the oxygen. No aspirator was needed in this experiment: the air began to enter the flask as soon as the stopcock was turned.

The air, before reaching the copper, was freed from carbon dioxide by means of caustic potash, and from water vapour by means of sulphuric acid. The results of many experiments gave the mean value:—

Oxygen 23 per cent, Nitrogen 77 per cent, by weight.

Compare this with the results of experiments similar to Experiment 30, which give the values:—

Oxygen 20·96 per cent, Nitrogen 79 per cent, by volume.

Experiment 82.—To prepare nitrogen from ammonium nitrite.

Set up the apparatus shown in fig. 72. Place a strong solution of ammonium nitrite in the flask. Heat the flask gently. Notice the effervescence due to the liberation of nitrogen.

Wait until the nitrogen has had time to displace the air from the flask. Then place the inverted gas-jar full of water on the shelf and collect the gas coming off. When two jars full of the gas have been collected in this way, remove the delivery-tube from the water. Then—not before—cease the heating.

Show that the gas collected is nitrogen by applying to it the various tests applied in Experiment 81.

Preparation.—1. Nitrogen may be prepared by removing the oxygen from an enclosed volume of air by means of iron or phosphorus. (See Experiments 31 and 32.)
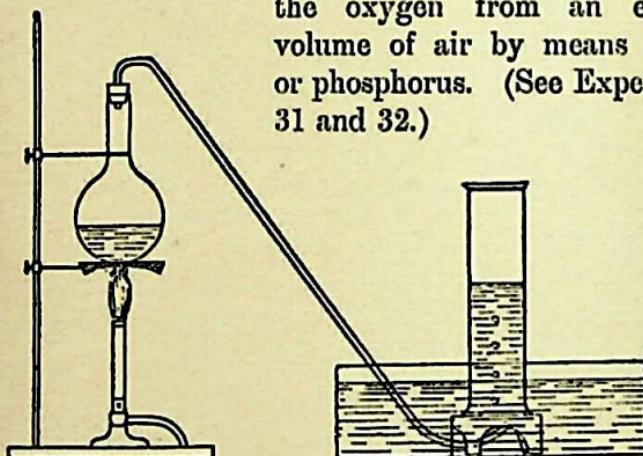
Fig. 72.—Preparation of Nitrogen from Ammonium Nitrite

2. Similarly the gas may be prepared by passing a current of air over red-hot copper turnings.

3. Nitrogen is usually prepared in the laboratory by heating ammonium nitrite. Ammonium nitrite is a salt which on heating splits up into nitrogen and water.

Properties.—Nitrogen is a colourless, odourless gas. It is slightly soluble in water, forming a neutral solution.

Nitrogen forms about 79 per cent (by volume) of the atmosphere. (See Chapter IV.) In Chapter IV the one property of the gas on which emphasis was laid was that the gas would not support the combustion of a taper.

Other gases which will not support the combustion of a taper have since been studied—for example, carbon dioxide, sulphur dioxide, and chlorine.

The great distinction between nitrogen and these gases lies in the fact that *they* will react chemically with many other substances, whereas nitrogen will not. The properties of nitrogen are negative properties: not what the gas *will* do, but what the gas will *not* do. There are very few elements with which nitrogen can be made to combine directly, and to bring about even these combinations requires a high temperature. We say the gas is inert or chemically inactive.

Most elements will combine with oxygen. Some combine at the ordinary temperature and others only on heating. Nitrogen will not combine with oxygen below 1000° C.

On strongly heating, nitrogen will combine with certain metals—for example, magnesium—forming nitrides.

History.—Nitrogen was discovered by Scheele, and independently by Rutherford, in 1772.

Rutherford isolated the gas from the atmosphere by burning carbon in an enclosed volume of air and absorbing by means of caustic potash the carbon dioxide produced.

NITRIC ACID

Experiment 83.—To find the effect of sulphuric acid upon saltpetre.

Place 20 grm. of saltpetre in a 250-cu.-cm. retort provided with a glass stopper. Take care that the salt does not lodge in the neck N of the retort (fig. 73). Pour 12 cu. cm. of concentrated sulphuric acid upon the saltpetre by means of a funnel. In this way the acid may be prevented from running down the neck of the retort.

Shake the retort slightly in order to mix the acid and salt.

Arrange the retort and the remainder of the apparatus as in fig. 73.

Gently heat the retort by means of the Bunsen burner. Collect the liquid which distils over in the flask F. Note that the flask is kept cool by a stream of cold water, and that the neck of the retort is thrust well into the flask. Collect a moderate quantity of the distillate for use in the next experi-

ments. Be very careful in working with this liquid, because it is a strong acid. Pour the hot liquid remaining in the retort into a dish before it solidifies in the retort.
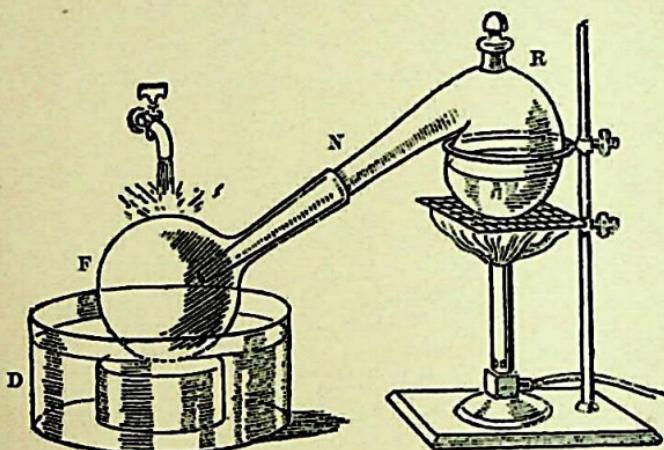
Fig. 73.—Preparation of Nitric Acid from Saltpetre

Experiment 84.—To examine the liquid which distils over from a mixture of saltpetre and sulphuric acid.

(i) Make a weak solution of the liquid by adding 1 cu. cm. of the liquid to 5 cu. cm. of water. Use the dilute solution for the following tests:—

    (a) Test the solution with litmus.

    (b) Pour a little of the solution upon sodium carbonate. Identify the gas evolved by means of lime-water, as in Experiment 58.

    (c) Pour a little of the solution upon a little zinc contained in a test-tube. Identify the gas evolved (see Experiment 40). These tests should indicate to you that the liquid is an acid. Now try to identify the acid.

(ii) Pour a few drops of the liquid collected (not the diluted liquid) upon a few pieces of copper contained in a test-tube. Warm the mixture. Compare the result with the results of

Experiment 49. Name the acid obtained when saltpetre is acted upon by sulphuric acid.

(iii) Heat a little dry saw-dust in an evaporating-dish until it is just ready to char. Then pour upon it a little of the concentrated nitric acid, the liquid prepared in the last experiment. Be careful not to stand too near the dish when adding the acid, as the reaction is often vigorous.

(iv) Notice the effect which a drop of the acid has upon the skin or finger-nail.

(v) Heat a little of the concentrated nitric acid in a small flask. Freshly prepared nitric acid is recommended for this test. Thrust a glowing splinter into the vapour. What happens?

(vi) Pour a little ferrous (iron) sulphate or green vitriol solution into a test-tube. Hold the test-tube in a slanting position and gently pour a few drops of nitric acid down the side of the test-tube. This will prevent the liquids from mixing. Notice the production of a brown ring where the liquids meet. This "brown-ring" test is used in testing for nitric acid or nitrates.

(vii) Add a few drops of nitric acid to a solution of indigo. What happens?

Preparation.—Nitric acid is prepared by distilling a nitrate with sulphuric acid. Potassium nitrate (saltpetre) or sodium nitrate (Chili saltpetre) is usually employed.

$$\left.\begin{array}{c}\text{potassium} \\ \text{nitrate}\end{array} + \begin{array}{c}\text{hydrogen} \\ \text{sulphate}\end{array}\right\} \text{form} \left\{\begin{array}{c}\text{potassium hydrogen} \\ \text{sulphate}\end{array} + \begin{array}{c}\text{hydrogen} \\ \text{nitrate.}\end{array}\right.$$
(sulphuric acid)   (nitric acid)
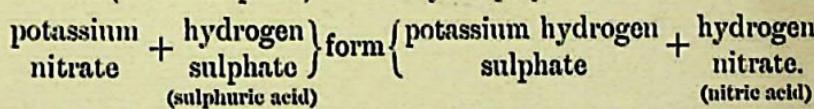
At a higher temperature the potassium hydrogen sulphate reacts with potassium nitrate to form nitric acid. The potassium hydrogen sulphate is changed to potassium sulphate.

$$\left.\begin{array}{c}\text{potassium} \\ \text{nitrate}\end{array} + \begin{array}{c}\text{potassium hydrogen} \\ \text{sulphate}\end{array}\right\} \text{form} \left\{\begin{array}{c}\text{potassium} \\ \text{sulphate}\end{array} + \begin{array}{c}\text{nitric} \\ \text{acid.}\end{array}\right.$$
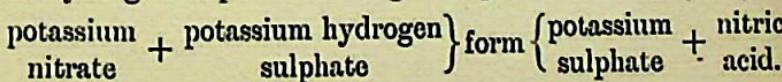
Properties.—Nitric acid is a colourless liquid having a density of 1·56. It fumes in air and boils at 86° C. The acid contains a high percentage of oxygen, and is easily de-

composed. The brown fumes of nitrogen peroxide which appeared in the retort in Experiment 83 were due to the decomposition of nitric acid by heat. These brown fumes dissolved in the nitric acid, which in consequence was coloured slightly yellow.

Light also brings about the same decomposition. Hence, on keeping, nitric acid turns yellow and oxygen is given off.

$$\left.\begin{array}{c}\text{nitric}\\\text{acid}\end{array}\right\}\begin{array}{c}\text{decomposes}\\\text{into}\end{array}\left\{\begin{array}{c}\text{nitrogen}\\\text{peroxide}\end{array}\right. + \text{oxygen} + \text{water}. \qquad (i)$$
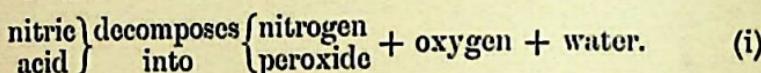
Nitric acid readily attacks (enters into chemical combination with) and dissolves nearly all metals. Gold and platinum are exceptions (see p. 83). A mixture of four volumes of hydrochloric acid and one volume of nitric acid will dissolve gold and platinum. This mixture is called "aqua regia". When gold is dissolved in aqua regia the hydrogen in the hydrochloric acid is oxidized to water by the nitric acid present. The chlorine combines with the metal, forming gold chloride.

The hydrogen set free when metals dissolve in nitric acid possibly brings about a change similar to that caused by heat and light, only much more quickly. Thus we may imagine—

$$\left.\begin{array}{c}\text{nitric}\\\text{acid}\end{array} + \text{copper}\right\}\text{form}\left\{\begin{array}{c}\text{copper}\\\text{nitrate}\end{array}\right. + \text{hydrogen}. \qquad (ii)$$

$$\left.\begin{array}{c}\text{nitric}\\\text{acid}\end{array} + \text{hydrogen}\right\}\text{form}\left\{\begin{array}{c}\text{nitrogen}\\\text{peroxide}\end{array}\right. + \text{water}. \qquad (iii)$$
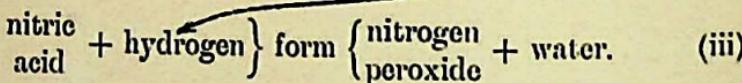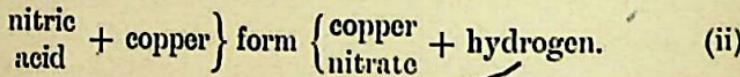
Compare (iii) with (i). They are identical except that in (iii) the hydrogen has combined with the oxygen to form an additional quantity of water. In (i) it was the heat which decomposed the nitric acid. In (iii) it is the attraction between the hydrogen and the oxygen which brings about the reduction of the nitric acid.

Nitric acid is a very strong oxidizing agent. Many examples of its oxidizing action have already been met with, e.g. the oxidation of (a) the carbon in wood into carbon

dioxide (Exp. 84 (iii)), (b) indigo into a colourless compound (Exp. 84 (vii)), (c) copper into copper nitrate (Exp. 84 (ii)).

If sulphur, phosphorus, or iodine be boiled with nitric acid the elements are oxidized into sulphuric acid, phosphoric acid, and iodic acid respectively. Iron and lead sulphides are oxidized to sulphates by the addition of nitric acid. Nitric acid rapidly attacks organic matter, that is, material which has come from a living thing. (See Experiment 84 (iv).) It is for this reason that a retort was used in the preparation of the acid. The nitric acid would have attacked the stopper (rubber or cork) necessary with a flask. Explosives are made by the action of nitric acid upon certain organic substances. For example, cotton is changed to gun-cotton and glycerol to nitro-glycerol, the active agent in dynamite, by the action of nitric acid.

The salts of nitric acid are called nitrates. Nitrates detonate (explode) if added to incandescent charcoal. This is due to the rapid oxidation of the carbon by the oxygen in the nitrate. Nitrates if heated alone are decomposed. Oxygen and oxides of nitrogen are evolved, and the metal generally remains as the oxide. (See Experiment 69, p. 117.)

Distribution.—Nitric acid occurs in nature in combination as nitrates. The most important natural nitrates are saltpetre (potassium nitrate) and Chili saltpetre (sodium nitrate). They are both valuable manures.

India was the main source of the world's supply of saltpetre until the discovery of the sodium nitrate deposits in Chili, Bolivia, and Peru. India now exports nitrates to the value of £280,000 per annum.

Production of Nitrates.—When organic matter decays, ammonia and ammonium compounds are produced. The ammonia is oxidized by bacteria (extremely minute living creatures) into nitric acid. This reacts with the potassium compounds present in the soil and forms potassium nitrate.

This process occurs very rapidly in hot and fairly dry countries like India, Persia, and Arabia, where the quantity of urine and other organic matters which find their way into

the soil is very great. The nitrates may crystallize out on the surface of the soil. Otherwise the soil must be extracted with water. The water is then evaporated and crystals of impure potassium nitrate are formed. The salt is purified by recrystallization.

Plants require nitrogen as part of their food. They cannot, however, assimilate (feed upon) the free nitrogen of the air. Combined nitrogen is necessary. This the plant obtains from the soil, often in the form of a nitrate.

As the nitrates in the soil are used up by the plant, they must be replaced if the soil is to remain fertile. This accounts for the use of nitrogenous manures. The manure provides the necessary compounds of nitrogen.

It is interesting to note that there are certain bacteria which live on the roots of plants, notably of the pea tribe, in a sort of partnership. These bacteria are able to bring about the combination of atmospheric nitrogen, so that the plant with which they live can assimilate it. The introduction of these bacteria into the soil, with a view to rendering it more fertile, has been tried with some amount of success.

It is imperative for the development of agriculture that a plentiful, cheap supply of combined nitrogen should be available. The natural supplies (saltpetre) will not last indefinitely. Hence the artificial production of combined nitrogen has received and is receiving attention. Two methods which are worked commercially are as follows:—

(i) Hydrogen and nitrogen are heated in the presence of finely divided iron. The iron brings about the combination of the hydrogen and nitrogen with the formation of ammonia (p. 153).

(ii) A current of air is passed through a powerful electric arc between copper tubes. The high temperature of the arc causes a *little* of the nitrogen and oxygen to combine, forming nitric oxide.

The nitric oxide combines with oxygen and forms nitrogen peroxide, which is absorbed by lime and water, forming calcium nitrate.

NITRIC OXIDE

When nitric acid is reduced by metals, various oxides of nitrogen and other substances are produced. The products of the reduction depend upon the metal used, the temperature of the reaction, and the concentration of the acid.

Of these products the easiest to prepare in a pure state is nitric oxide.

Experiment 85.—To prepare nitric oxide and examine its properties.

Fit up the apparatus shown in fig. 74. Place some copper
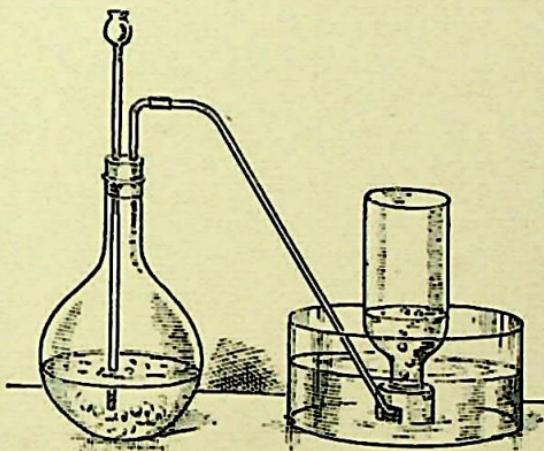
Fig. 74.—Preparation of Nitric Oxide from Nitric Acid

turnings in the flask and pour dilute nitric acid down the funnel. The reaction between the copper and the nitric acid generally takes place without heating. If necessary, the flask must be warmed gently.

Notice that the flask at first fills with a reddish-brown gas (nitrogen peroxide). When the gas in the flask is colourless (nitric oxide), proceed to collect two or three jars of the gas.

After collecting the required amount of the gas, do not let the nitric oxide escape from the delivery-tube into the air, as the fumes produced are injurious. Either dilute the acid

remaining in the flask with sufficient water to stop the reaction or place the flask in a fume-closet.

Examine the gas according to the usual scheme (p. 46), but reserve one jar full of the gas for use in Experiment 86. Perform the following experiments with the other specimens of the gas.

(a) Examine the solubility of the gas in iron sulphate solution (ferrous sulphate). Note the change in colour of the solution.

(b) Try to burn sulphur and phosphorus in the gas in turn. The sulphur and phosphorus should be well alight before being placed in the gas.

(c) If you have not already done so, notice the change in the colour of the gas when it comes into contact with the air.

Preparation.—Nitric oxide is usually prepared by the action of dilute nitric acid upon copper.

$$\left.\begin{matrix}\text{Nitric}\\\text{acid}\end{matrix} + \text{copper}\right\} \text{form} \left\{\begin{matrix}\text{copper}\\\text{nitrate}\end{matrix} + \text{water} + \begin{matrix}\text{nitric}\\\text{oxide.}\end{matrix}\right.$$
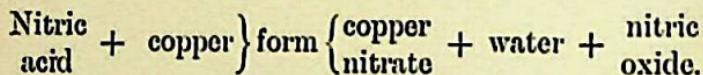
Sulphuric acid and potassium nitrate may, if desired, be used in place of the nitric acid.

Properties.—Nitric oxide is a colourless gas. It is slightly soluble in water, forming a neutral solution. The gas is, however, very soluble in a solution of iron sulphate (ferrous sulphate), forming a dark-brown solution. Thus in the "brown-ring" test for nitric acid, when ferrous sulphate is added to nitric acid the nitric acid oxidizes the ferrous sulphate and forms ferric sulphate. In doing so, the nitric acid is reduced to nitric oxide. The nitric oxide dissolves in the ferrous sulphate present, and forms a brown ring. (See Experiment 84 (vi).)

Nitric oxide combines with oxygen at ordinary temperatures, forming nitrogen peroxide. Nitric oxide is fairly readily decomposed into its elements. Brightly burning phosphorus will decompose the gas and burn in the oxygen set free. Neither burning sulphur nor glowing charcoal raises the tem-

perature of the gas high enough to decompose it. Consequently neither carbon nor sulphur will burn in nitric oxide. Nitric oxide may be synthesized by exploding a mixture of nitrogen and oxygen in a eudiometer. The combination of the elements takes place very slowly.

NITROUS OXIDE

When nitric acid is neutralized by ammonia, ammonium nitrate is formed.

$$\text{Nitric acid} + \left. \begin{matrix} \text{ammonium} \\ \text{hydroxide} \end{matrix} \right\} \text{form} \left\{ \begin{matrix} \text{ammonium} \\ \text{nitrate} \end{matrix} \right. + \text{water.}$$
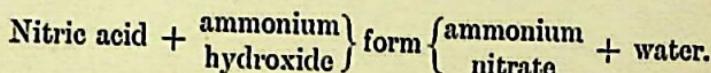
We will next study the effect of heat upon ammonium nitrate.

Experiment 86.—To prepare nitrous oxide and to examine its properties.

(i) Fit up the apparatus shown in fig. 72. The use of a wide delivery-tube is recommended. Place 20 grm. of powdered ammonium nitrate in the flask.

Nitrous oxide is rather soluble in cold water, so that the trough and gas-jars must be filled with warm water.

Heat the ammonium nitrate *very gently* until it melts, and bubbles of gas are given off. If heated too strongly the ammonium nitrate will froth up and overflow into the delivery-tube.

When the air has been expelled from the apparatus by the nitrous oxide, collect two or three jars full and one jar about half full of the gas.

Remove the delivery-tube from the water, and stop the heating before all the salt is decomposed.

(ii) Examine the gas according to the usual scheme (p. 46). Also perform the following experiments with the gas:—

(a) Thrust a glowing splinter of wood into the gas. (Is the splinter rekindled?)

(b) Heat a little sulphur in a deflagrating-spoon until it boils. Lower the lighted sulphur into the gas. (What

happens?) Cautiously smell the gas produced in the gas-jar, and try to identify it.

(c) Ignite a small piece of phosphorus in a deflagrating-spoon. Introduce the burning phosphorus into a jar of nitrous oxide.
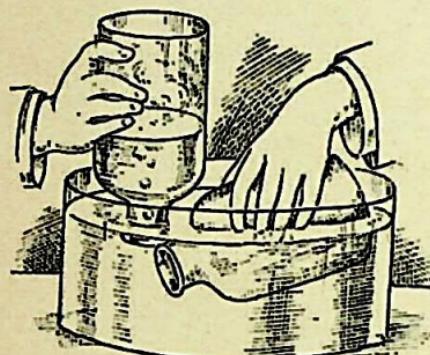
Fig. 75.—Transferring a Gas from one Vessel to another

(d) Try to burn fine iron wire in the gas. For instructions how to proceed refer to Experiment 35 (vii).

(e) Try to burn a piece of carbon in the gas, and endeavour to identify the product of the reaction.

(f) Take the jar full of nitric oxide kept from Experiment 85, and pour some of the nitric oxide into the jar half full of nitrous oxide (fig. 75). Are red fumes produced?

Preparation.—Nitrous oxide is prepared by heating ammonium *nitrate*. The reaction should be compared with that which takes place when ammonium *nitrite* is heated. (See p. 137.) On heating,

Ammonium nitrate forms nitrous oxide + water.

Ammonium nitrite forms nitrogen　　 + water.

Properties.—Nitrous oxide is a colourless gas with a faint smell. The gas is fairly soluble in ice-cold water, but only half as soluble in water at 25° C. The solution is neutral, so that nitrous oxide is not an anhydride.

Nitrous oxide is readily decomposed by heat into its elements—nitrogen and oxygen. It will therefore support combustion almost as well as oxygen. E.g. carbon, iron, and phosphorus will burn in nitrous oxide, forming respectively carbon dioxide, iron oxide, and phosphorus pentoxide. Well-lighted sulphur burns in nitrous oxide, and forms sulphur

dioxide. If, however, the sulphur is burning only feebly, the heat produced by the burning sulphur is not sufficient to decompose the nitrous oxide. Under these circumstances the sulphur will not burn in the gas. In every case before combustion can proceed the nitrous oxide must be decomposed by the burning substance.

The properties of nitrous oxide are thus seen to be very similar to those of oxygen. Like oxygen the gas will relight a glowing splinter of wood. Nitrous oxide can be distinguished from oxygen by its effect upon nitric oxide. When oxygen is mixed with nitric oxide, red fumes of nitrogen peroxide are formed. No such change occurs when nitrous oxide and nitric oxide are mixed. Nitrous oxide, if inhaled for a short time, causes insensi-
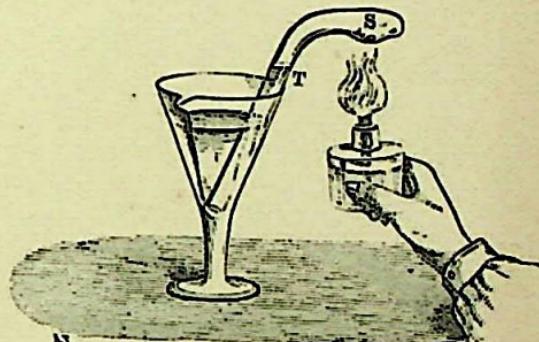
Fig. 76.—Composition of Nitrous Oxide

bility. For this reason it is used as an anæsthetic. From the symptoms attending its use it is sometimes called "laughing gas".

Composition.—The composition of the gas may be determined as follows:—

(i) A piece of sodium is placed in the horizontal portion of the bent tube T (fig. 76). The tube is then partly filled with nitrous oxide collected over mercury.

On heating the sodium it burns in the nitrous oxide and forms sodium oxide. Nitrogen is thus set free in the tube. It is found that the volume of nitrogen so liberated occupies the same volume as was occupied by the nitrous oxide.

(ii) Nitrous oxide is collected over mercury in a eudiometer (fig. 42). The volume of gas collected is measured, and a little more than an equal volume of hydrogen is added to

it. On igniting the mixture by means of an electric spark (see p. 65) the hydrogen and oxygen combine to form water.

The eudiometer then contains nitrogen and some unused hydrogen.

The hydrogen may be removed by introducing more than enough oxygen required to oxidize the hydrogen to water— say one-third of the volume of the gases in the eudiometer— and "sparking" again.

The eudiometer then contains nitrogen and some unused oxygen.

The oxygen is absorbed by introducing a solution of pyrogallic acid into the eudiometer. Oxygen is soluble in an alkaline solution of pyrogallic acid. The eudiometer then contains nitrogen. *This nitrogen will be found to occupy the same volume as the nitrous oxide.*

History.—Nitrous oxide was discovered by Priestley in 1772.

AMMONIA

Experiment 87.—To find the effect of heat upon a mixture of sal-ammoniac (ammonium chloride) and caustic soda.

(i) Place a small quantity of ammonium chloride in a test-tube and cover it with caustic soda solution. Heat the mixture in a Bunsen burner and cautiously smell the gas evolved.

Can you recognize the gas by its smell?

Test the gas with red litmus. Dip a glass rod into hydrochloric acid and hold the wet rod in the escaping gas. Notice the fumes which form.

The gas obtained by the action of caustic soda upon ammonium chloride is called ammonia.

(ii) Repeat the experiment with other ammonium salts— ammonium sulphate, ammonium nitrate—using either caustic soda, caustic potash, or lime.

Is ammonia evolved in every case?

Experiment 88.—To prepare ammonia and to examine its properties.

(i) Fit up the apparatus shown in fig. 77. The flask F contains a mixture of ammonium chloride and lime which has been ground and intimately mixed. The drying-tower T contains lumps of lime to dry the gas. The gas is collected by upward displacement of air in the gas-jar J.

Heat the mixture in F by means of the Bunsen burner.
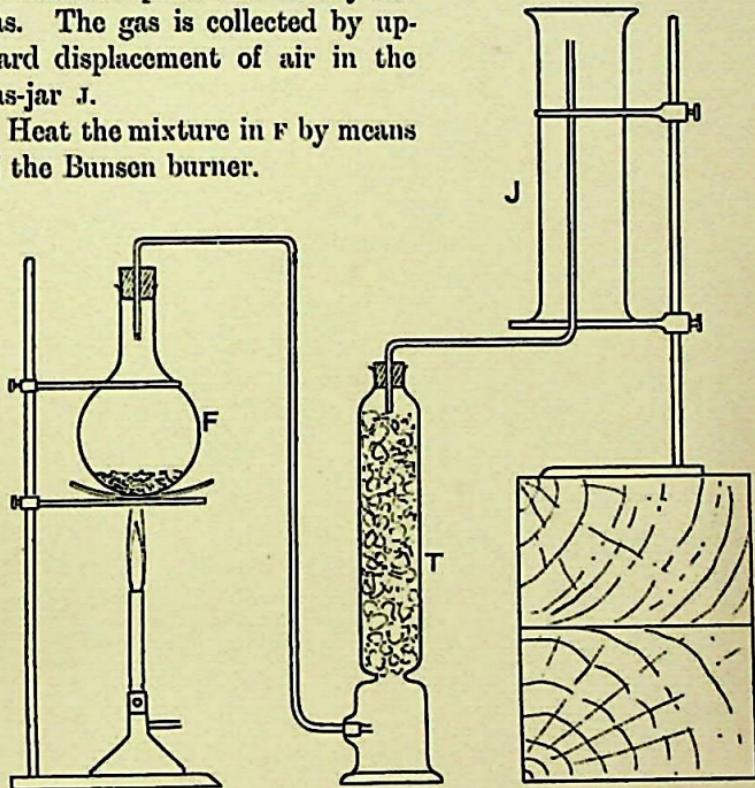
Fig. 77.—Preparation of Ammonia from Ammonium Chloride

A piece of damp red litmus-paper placed at the mouth of the jar will indicate when the jar is full of ammonia. Collect three jars full and a flask full [see below (a)] of the gas, and—

(ii) Examine the gas according to the usual scheme (p. 46). When testing the solubility of the gas, the gas-jar should be covered with a duster wrapped round and round the jar to protect the hand in case of a breakage, because the water
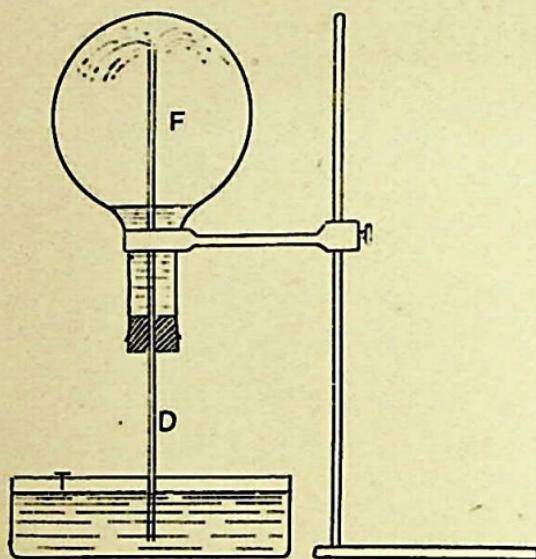
Fig. 78.—Solubility of Ammonia in Water

rushes up into the gas-jar with great force if the jar is quite full of ammonia.

Also perform the following experiments with the gas to illustrate its properties:—

(*a*) Fit up the flask F on the stand (fig. 78) and fill it with dry ammonia. If desired, the ammonia for this and the following experiment may be obtained by heating a strong aqueous solution of ammonia in the flask F (fig. 77). Fill the trough T with water coloured red with litmus solution. Rinse out the tube D with water, and when the flask is quite full of ammonia insert the stopper and tube D. The ammonia dissolves in the water, which forms a fountain in F. The alkaline nature of the ammonia is indicated by the change in colour of the litmus.

(*b*) Arrange the apparatus shown in fig. 79. Fit a small burner of platinum-foil on F to prevent fusion of the end of the tube A during the experiment. A slow current of oxygen is passed through tube O and a current of ammonia
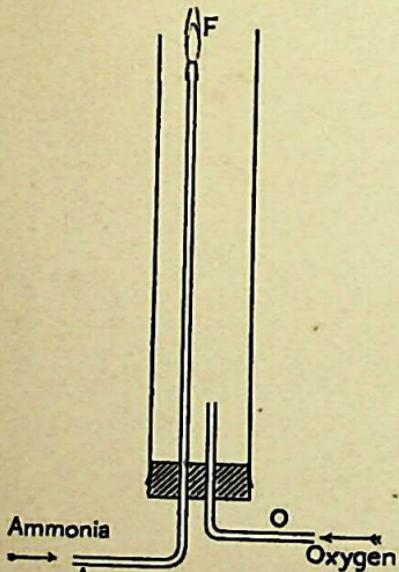
Fig. 79.—Ammonia Burning in Oxygen

Ammonia

Oxygen

through tube A. The wide glass tube serves to confine the ammonia round the flame at F. The ammonia can be ignited as it issues from F.

(c) Place a small beaker on a drop of water upon a block of wood. In the beaker place a little strong ammonia solution. Blow a rapid current of air from a pair of bellows through the ammonia. It will be found that the water on the wood changes to ice and freezes the beaker to the wooden block.

(d) Prepare specimens of ammonium chloride and ammonium sulphate by neutralizing hydrochloric acid and sulphuric acid respectively with a solution of ammonia in water, and concentrating the solution thus obtained.

Preparation.—(i) Ammonia is formed when organic matter containing nitrogen is heated, more especially when it is heated with lime or caustic soda or soda lime, that is, lime slaked with caustic soda solution. The objectionable smell which is noticed when hair and feathers are burned is due to the formation of impure ammonia.

(ii) The usual laboratory method of preparation is to heat ammonium chloride with twice its weight of lime.

$$\left.\begin{matrix} \text{ammonium} \\ \text{chloride} \end{matrix} + \begin{matrix} \text{calcium} \\ \text{oxide} \\ \text{(lime)} \end{matrix}\right\} \text{form} \left\{\begin{matrix} \text{calcium} \\ \text{chloride} \end{matrix} + \text{ammonia} + \text{water.}\right.$$
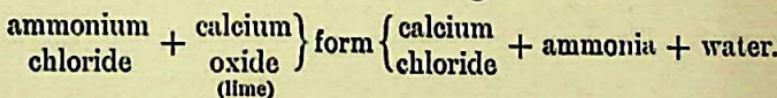
(iii) Certain metals, such as magnesium and aluminium, when heated in nitrogen or ammonia form nitrides, that is, compounds of the metals and nitrogen. On the addition of water to a nitride it decomposes into ammonia and an oxide of the metal.

$$\left.\begin{matrix} \text{magnesium} \\ \text{nitride} \end{matrix} + \begin{matrix} \text{water} \\ \text{(hydrogen oxide)[1]} \end{matrix}\right\} \text{form} \left\{\begin{matrix} \text{magnesium} \\ \text{oxide} \end{matrix} + \begin{matrix} \text{ammonia.} \\ \text{(hydrogen nitride)} \end{matrix}\right.$$
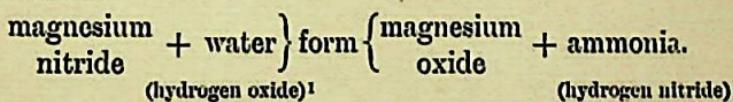
(iv) The chief source of our supply of ammonia is from the ammoniacal liquor from gasworks and from blast-furnaces. When coal is distilled in the making of gas, ammonia is

[1] The aim in writing "water" as "hydrogen oxide" and "ammonia" as "hydrogen nitride" is to induce the student to look upon reactions, wherever possible, as cases of double decomposition. (See p. 112.)

formed. The coal-gas is cooled by passing it through iron pipes. In these pipes ammonium hydroxide and ammonium salts condense and the solution flows into a well. To obtain ammonia, the solution of ammonia and ammonium salts is treated with lime. The ammonia is then absorbed in sulphuric acid to form ammonium sulphate.

Properties. —Ammonia is a colourless gas with a characteristic pungent odour. It is about half as heavy as air.

The gas is extremely soluble in water, and forms an alkaline solution possessing basic properties. (See p. 86.) This solution is commonly called "ammonia". By heating a solution of the gas the whole of the ammonia may be removed from the solution. If a solution of ammonia in water is added to a soluble salt of copper, iron, lead, magnesium, &c., a precipitate is obtained which is exactly similar to the precipitate given when sodium hydroxide is used in place of the solution of ammonia. Hence the aqueous solution of ammonia is called ammonium hydroxide.

Now all other hydroxides are compounds of water with a metallic oxide (see p. 52). A solution of ammonia is therefore looked upon as the hydroxide of an imaginary metal called ammon*ium*. Like all other hydroxides, ammonium hydroxide neutralizes acids to form salts and water. These facts are summarized below. In reading them distinguish carefully between the gas "ammonia", and the hypothetical metal "ammonium".

ammonia	+	water	form	ammonium hydroxide			(i)
ammonium hydroxide	+	copper sulphate	"	ammonium sulphate	+	copper hydroxide	(ii)
sodium hydroxide	+	copper sulphate	"	sodium sulphate	+	copper hydroxide	(iii)
ammonium hydroxide	+	hydrochloric acid	"	ammonium chloride	+	water	(iv)
ammonia	+	hydrochloric acid	"	ammonium chloride			(v)

Ammonia may readily be liquefied at ordinary temperatures by increasing the pressure on the gas to about seven times the ordinary atmospheric pressure. Liquid ammonia boils at −33° C., and in doing so, like all other liquids, absorbs a certain amount of heat (latent heat).[1]

Advantage is taken of this absorption of heat in the use of liquid ammonia as a refrigerating (cooling) agent. Gaseous ammonia is compressed and liquefied. It is then allowed to " boil " by reducing the pressure. In boiling, it cools tanks of salt-water so that cans of fresh-water placed in the cold salt-water are frozen, and artificial ice is thus produced.

In cold-storage rooms used for the preservation of perishable food-stuffs the cold salt-water circulates through pipes in the room, and so reduces the temperature of the room.

The fuming of ammonia in the presence of hydrochloric acid (see Experiment 73) is due to the formation of ammonium chloride (see (v), p. 154). The combination may be strikingly shown, as in Experiment 73 (ii), p. 123. Ammonia is a non-supporter of combustion and will not burn in air. It will, however, burn in oxygen, forming amongst other products nitrogen and water. This points to the fact that nitrogen and hydrogen are amongst the elements of which ammonia is composed.

Composition of Ammonia.

(i) A long tube, T, fig. 80, is sealed at one end and closed by a stopcock C. The projection from C to A serves as a funnel. Fill the tube with chlorine collected over water and close the stopcock. Stand the tube of chlorine, C uppermost, in the cylinder of water D, and fill the funnel A with a strong solution of ammonia. Admit the ammonia a little at a time into the tube T by momentarily turning the stopcock C. Notice the flashes of light which occur as the ammonia combines with the chlorine.

ammonia + chlorine form hydrochloric acid + nitrogen

hydrochloric acid + ammonia form ammonium chloride.
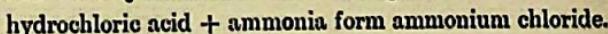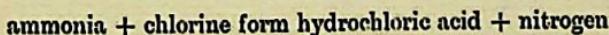
[1] See page 220 of *A Course in Physics*, published by Messrs. Blackie & Son.

When the reaction ceases, empty out the remaining ammonia from the funnel and fill the funnel with dilute sulphuric acid. Invert the tube in a dish of dilute sulphuric acid. Open the stopcock and the acid will enter the tube and unite with the excess of ammonia previously added. The tube then contains nitrogen (see above). The volume of this
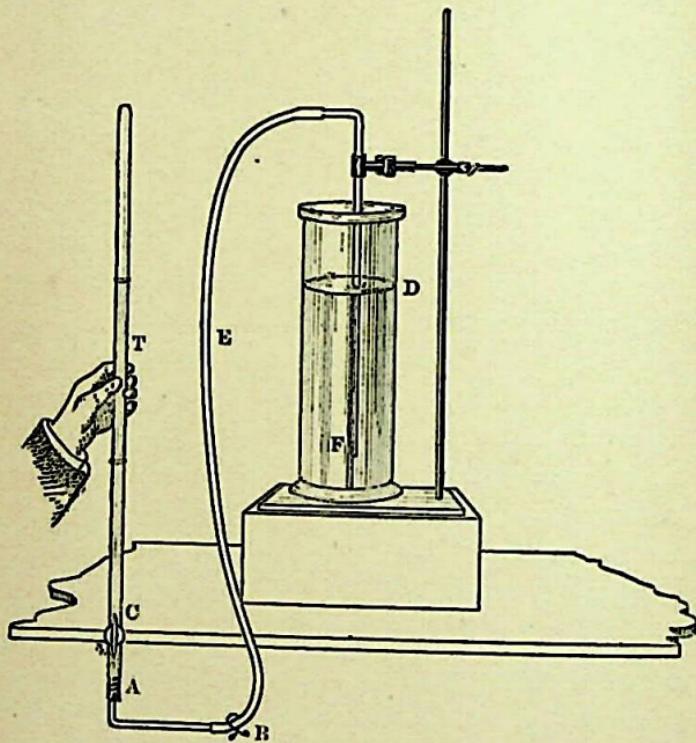
Fig. 80.—Composition of Ammonia

nitrogen must now be measured at atmospheric pressure and temperature, so that it may be compared with the volume of chlorine employed.

Close the stopcock and invert the tube. Fill the funnel and the tubes E F with water, and close the clip B. Insert the cork A into the funnel and open the clip B. There should then be no air between C and F. Open the stopcock C and level the water surfaces in T and D.

It will be found that the tube is exactly one-third full of

nitrogen. Hence we conclude that 3 volumes of hydrogen and 1 volume of nitrogen combine to form ammonia, for we already know (see p. 133) that 1 volume of hydrogen unites with 1 volume of chlorine to form hydrochloric acid.

(ii) The composition of ammonia can also be determined by passing the dry gas over heated copper oxide. The oxygen of the copper oxide unites with the hydrogen in the ammonia to form water, so that the copper oxide is reduced to copper. This water is absorbed by calcium chloride in a series of drying-tubes. One-ninth of the increase in weight of the calcium chloride tubes is the weight of hydrogen in the decomposed ammonia (see p. 73).

The nitrogen set free when the hydrogen in the ammonia is oxidized to water is collected and its weight determined.

Exact experiments, the method of which is briefly sketched above, show that 1 grm. of hydrogen combines with 4·67 grm. of nitrogen to form ammonia.

Occurrence.—A little ammonia is found in the atmosphere. It is also produced in the soil when organic matter decays.

History.—Ammonia has been known from very early times. The preparation of the gas from ammonium chloride and lime was first demonstrated by Priestley in 1774. He collected the gas over mercury. The composition of the gas was established about twelve years later.

QUESTIONS ON CHAPTER XIV

1. How would you prepare a specimen of nitric acid in the laboratory, and how could you prove it to be nitric acid? Give a short description of how nitrates found in the soil are formed. (O. L.)

2. How is nitrous oxide prepared, and what are its characteristic properties? How would you distinguish it from oxygen gas? (O. L.)

3. Describe how air can be analysed, both by weight and by volume,

4. How would you distinguish experimentally between air, nitrogen, oxygen, and nitric oxide?

5. Describe the preparation and properties of nitric oxide. Account for the effects observed when this gas is slowly passed into a jar partly filled with air, standing over water. (C. L.)

6. By what experiments would you distinguish between nitric oxide and a mixture of equal volumes of nitrogen and oxygen? (C. L.)

7. Describe the preparation of nitric acid. Show by describing two experiments that nitric acid is an oxidizing agent. (C. L.)

8. What are the chief properties of nitric acid? (C. L.)

9. Describe two experiments by which you would show that there is nitrogen in ammonia. Describe any other experiments on ammonia gas which you have seen or performed. (O. L.)

10. How is dry ammonia prepared? Describe the chemical changes which take place when ammonia reacts with (a) a solution of ferric chloride, (b) nitric acid, (c) sulphuric acid. (C. L.)

CHAPTER XV

SULPHUR AND ITS COMPOUNDS

SULPHUR

The following properties of sulphur have already been

obtained in previous chapters.
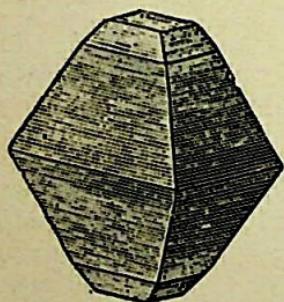
Sulphur is a pale-yellow, brittle solid, without taste or smell. It is insoluble in water, but dissolves in carbon bi-sulphide, from which it crystallizes out in the form of octahedra (fig. 81). Sulphur burns in oxygen (or air) and forms a colourless acid gas called sulphur dioxide, which when dissolved in water forms sulphurous acid.

Experiment 89.—To study the effect of heat upon sulphur.

(i) Heat some sulphur in an evaporating-dish, using a small flame. If a test-tube is used instead of an evaporating-dish, it should be held in a test-tube holder, as the tube gets very hot and the sulphur often takes fire at the mouth of the test-tube. Notice that the sulphur melts (at 120° C.) to a light yellow mobile liquid. Continue the heating until the sulphur begins to boil. Write down the changes in the colour of the sulphur and also the changes in its viscidity, or the ease with which the liquid will flow.

Notice also the colour of the vapour produced when the liquid boils. While the sulphur is boiling, hold a test-tube containing cold water in the vapour. Observe the crystals of sulphur which are deposited on the glass. Sulphur formed in this way is called *flowers of sulphur*.

Remove the flame, and as the sulphur cools repeat the observations upon its colour and viscidity.

(ii) Melt a large quantity of sulphur in an evaporating-dish by means of a Bunsen burner. As soon as the mass is melted turn out the flame. Allow the liquid sulphur to cool until a thin crust of solid sulphur forms on the top of the liquid. Then pierce this crust with a hot iron rod, and quickly pour out the liquid sulphur from under the crust into any suitable vessel. Observe the shape of the crystals of sulphur left in the evaporating-dish. [What shape are they?] This form of sulphur is called *prismatic sulphur*.

(iii) Heat some sulphur as in (i). When it is of a dark-red colour and liquid enough to flow, pour it in a thin stream into a beaker of cold water. Examine the solid formed when sulphur is cooled rapidly in this way. [Is it crystalline and brittle?] This form of sulphur is called *plastic sulphur*. Keep a piece of this plastic sulphur for some days, and observe the change it undergoes. For preparing large quantities of plastic sulphur the apparatus shown in fig. 82 is convenient.

Liquid Sulphur.—Sulphur melts at 120° C., and forms a light-yellow mobile liquid. As the melted sulphur is heated

further it darkens in colour, until it forms a dark-red mass. At the same time it behaves differently from most liquids. Liquids usually become "thinner" (less viscid) when heated, whereas sulphur first becomes very much "thicker" (more viscid), and on continued heating becomes quite liquid again.

Forms of Sulphur.—Sulphur exists in three forms.

(i) *Octahedral sulphur.*—When sulphur crystallizes at low temperatures it does so in the form of octahedra (see fig. 81). The density of octahedral sulphur is 2·07. This is the form in which sulphur crystallizes out from solution in carbon bisulphide. The fact that the other forms ultimately change into the octahedral variety probably accounts for the occurrence of sulphur in nature in the form of octahedra.

Fig. 82.—Preparation of Plastic Sulphur

(ii) *Prismatic sulphur.*— When sulphur crystallizes at or above 100° C. it does so in the form of oblique prisms, and is called prismatic sulphur. The density of prismatic sulphur is 1·96. Prismatic sulphur soon changes slightly in colour, and becomes more brittle and opaque. The density at the same time increases to 2·07, indicating that the sulphur has changed from the prismatic form to the octahedral variety.

(iii) *Amorphous sulphur.*—When boiling sulphur is rapidly cooled it solidifies into a tough elastic substance rather like india-rubber. Such sulphur is known as *plastic sulphur*. While in this state sulphur is insoluble in carbon bisulphide. Plastic sulphur changes to the octahedral form if kept for a few days. The change can be effected in a few minutes by heating plastic sulphur to 100° C., or by stretching and working it in the hands.

The two well-known forms of sulphur—*flowers of sulphur*

and *milk of sulphur*—consist mainly of octahedral sulphur, and therefore are not special forms of sulphur in the same sense as are the varieties just described.

Milk of sulphur is a pale-yellow, almost white, form of sulphur in a very fine state of subdivision. It may be prepared by boiling some slaked lime with water and sulphur for some time. A reddish solution of calcium sulphides will be formed.

If the solution be decanted, and to it a little hydrochloric acid be added, milk of sulphur will be precipitated.

Allotropy.—The physical properties of the three forms in which sulphur exists are tabulated below:

	Octahedral Sulphur.	Prismatic Sulphur.	Plastic Sulphur.
Form ... ... {	octahedral crystals	prismatic crystals	amorphous solid.
Colour	lemon-yellow	amber-yellow	amber-yellow.
Melting-point ...	115° C.	120° C.	not well defined.
Malleability ...	brittle	brittle	plastic.
Solubility in carbon bisulphide ... }	soluble	soluble	insoluble.

At first sight it would seem as if it was not *one* element but three somewhat similar elements which were under consideration.

When, however, a specified weight of any of these three forms of sulphur is burnt in oxygen, *the sulphur dioxide produced weighs exactly the same in each case.* This indicates that each of the three forms is sulphur and nothing else than sulphur.

Also, if a certain weight of prismatic sulphur or of plastic sulphur is kept until it changes to octahedral sulphur, there is *no change in weight.* This, therefore, is a case of *an element which can exist in distinct forms with different properties.* The forms are spoken of as *allotropic forms* and *the property of the*

(0.729)

element in virtue of which it assumes these forms *is called allotropy*.

Purification of Sulphur.—Sulphur occurs naturally mixed with clay, sand, and other minerals (sulphur-ore). To obtain the sulphur from the ore, a large fire is made on a sloping floor, using sulphur-ore instead of coal. Some of the sulphur burns to sulphur dioxide, and the heat so produced melts the remainder of the sulphur, which flows away in a fairly pure condition. Sulphur is used as fuel in this process because it is so plentiful, and therefore cheaper than wood or coal.

The crude sulphur thus obtained is further purified by distilling it from iron retorts. The vapour passes into large brick chambers, where it condenses on the walls as *flowers of sulphur*. When the walls get hot the sulphur collects at the bottom of the chambers as a liquid. This liquid is then run off through an opening and collected in wooden moulds, in which it solidifies as roll sulphur.

Affinity of Sulphur for Metals.

Experiment 90.—(i) Boil some sulphur in a test-tube. Introduce a spiral of fine copper wire or foil into the vapour. Notice that the copper burns in the sulphur vapour. Examine the grey substance formed. It is a compound of copper and sulphur, and is called *copper sulphide*.

(ii) Repeat the experiment, using tin instead of copper. *Tin sulphide is formed.*

(iii) In a mortar grind up a little mercury with one-sixth of its weight of sulphur. *Black mercury sulphide is produced.*

(iv) Place a little silver-foil and some sulphur in a crucible. Place the lid on the crucible. Heat the crucible and its contents until the smell of burning sulphur is no longer noticeable on raising the lid. Add more sulphur, and heat as before. The crucible then contains a compound of silver and sulphur called *silver sulphide*.

These experiments illustrate the great affinity which exists between sulphur and the metals. In fact, sulphur forms compounds with almost all elements. At ordinary temperatures mercury and sulphur combine to form mercury sulphide, and

silver and sulphur combine to form silver sulphide. This latter fact accounts for the blackening of articles of silver left in contact with substances like indiarubber and matches which contain sulphur.

Distribution.—Sulphur is widely distributed in vast quantities, both as free sulphur in volcanic districts and in combination as sulphides. Sicily and Iceland are the main sources of the supply of free sulphur. Galena (lead sulphide), pyrites (iron sulphide), and copper pyrites (copper and iron sulphides) are sources of supply of both the metal and sulphur.

HYDROGEN SULPHIDE

Effect of Acids upon Sulphides.

Experiment 91.—(i) Add a small piece of iron sulphide to a little hydrochloric or sulphuric acid in a test-tube. Notice the effervescence which occurs. The gas given off is poisonous, and should be smelled with caution. It is called *hydrogen sulphide or sulphuretted hydrogen.*

(ii) Repeat (i), using sodium sulphide, zinc sulphide, copper sulphide, and mercury sulphide. Warm the acid if necessary. [Do all these sulphides yield sulphuretted hydrogen on treatment with acid?]

Fig. 83.—Kipp's Apparatus

Preparation.—Hydrogen sulphide or sulphuretted hydrogen
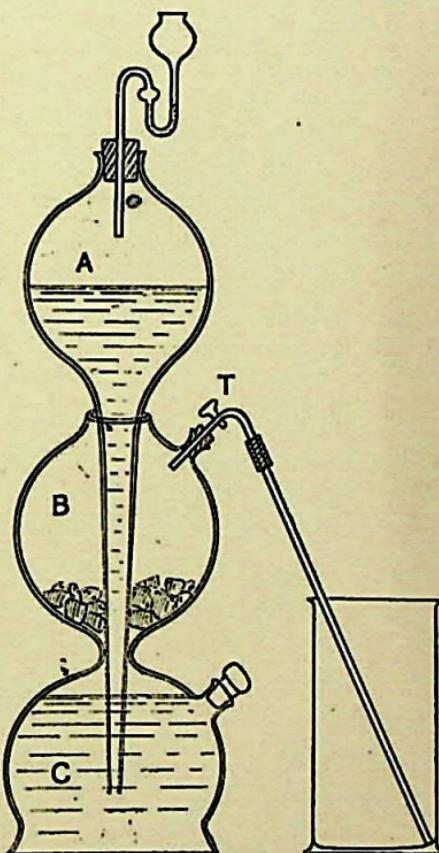
may be prepared by *the action of hydrochloric or sulphuric acid* on sodium sulphide, zinc sulphide, or *iron sulphide*. Iron sulphide is generally used because of its cheapness. The gas may be prepared in an apparatus similar to that used for the preparation of chlorine. Like chlorine, it is heavy enough to be collected by downward displacement as in fig. 64. Hydrogen sulphide is constantly needed, in small quantities, in the laboratory, and many types of apparatus have been designed to supply the need. Kipp's apparatus (fig. 83) is perhaps the most suitable. The bulb B is charged with iron sulphide in large pieces. The tap T is opened and hydrochloric acid is poured into A until it fills C and covers the iron sulphide in B. On turning off the tap the pressure of the hydrogen sulphide generated in B drives the acid into C and A. The removal of the acid from B causes the evolution of the gas to cease until the pressure of the gas in B is reduced by drawing off some of the gas by means of T, when the acid from C will again enter B.

$$\left.\begin{array}{c}\text{ferrous}\\\text{sulphide}\end{array} + \begin{array}{c}\text{hydrochloric}\\\text{acid}\end{array}\right\} \text{form} \left\{\begin{array}{c}\text{ferrous}\\\text{chloride}\end{array} + \begin{array}{c}\text{hydrogen}\\\text{sulphide.}\end{array}\right.$$
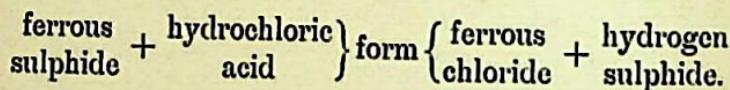
Experiment 92.—To prepare hydrogen sulphide and to examine its properties.

(i) Use Kipp's apparatus, and collect several jars full or test-tubes full of the gas by downward displacement (fig. 83).

(ii) Examine the gas according to the usual scheme (p. 46). In addition, perform the following experiments which illustrate other properties of the gas.

(*a*) Pass hydrogen sulphide direct from the Kipp's apparatus through a little concentrated sulphuric acid in a test-tube. (The delivery-tube must of course dip *into* the acid.) Notice the deposit of sulphur which forms. The hydrogen in the hydrogen sulphide unites with some of the oxygen in the sulphuric acid—reducing the acid to sulphur*ous* acid—and the sulphur in the hydrogen sulphide is thus set free. For this reason, sulphuric acid cannot be used to dry hydrogen sulphide. Calcium chloride is sometimes

used, although hydrogen sulphide attacks this salt with the formation of calcium sulphide. Phosphorus pentoxide is more suitable as a drying agent for the gas.

(*b*) Bring a jar of chlorine mouth to mouth with a jar of sulphuretted hydrogen. Notice the deposit of sulphur. The residual gas may be dissolved in a little water and tested for hydrochloric acid.

(*c*) Allow an aqueous solution of hydrogen sulphide— made by passing the gas through a test-tube full of water— to stand for a few days. The hydrogen sulphide in solution is oxidized, especially in the light, into water and sulphur.

Properties of Hydrogen Sulphide.

Hydrogen sulphide is a colourless gas with a sweetish taste and an odour like that of rotten eggs. It is poisonous. The gas is fairly soluble in water and forms an acid solution. The solution is a weak solution of the acid hydrogen sulphide, and is sometimes called hydrosulphuric acid. Unlike a solution of hydrochloric acid gas, the whole of the hydrogen sulphide may be driven out of the solution by boiling.

The acid nature of hydrogen sulphide is illustrated by the facts that the gas—

(i) Is rapidly absorbed by lime, forming calcium hydrosulphide.

(ii) Reacts with iron hydroxide to form iron sulphide.

acid	+.	*base* form a *salt*	+ *water*
hydrogen sulphide +	calcium hydroxide form	calcium sulphide +	water
(sulphuretted hydrogen)			
hydrogen sulphide +	iron hydroxide form	iron sulphide	+ water.
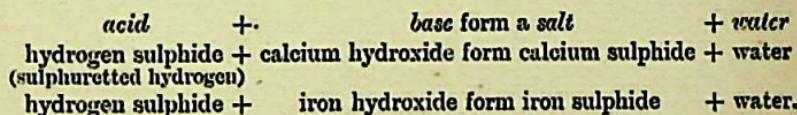
(iii) The hydrogen of hydrogen sulphide can be displaced by metals. For example:

. The gas attacks *silver* at ordinary temperatures, forming silver sulphide. This explains why silver articles are blackened readily by the air in towns. Copper, mercury, tin, iron, and most other metals are acted upon by hydrogen sulphide with the formation of sulphides of these metals. The action takes place more readily if the metals are heated.

Hydrogen sulphide will not support combustion, but the gas

burns in air, forming water and sulphur dioxide. If burnt in a limited supply of air only the hydrogen burns, and the sulphur is deposited.

Hydrogen sulphide is a reducing agent. The gas is not very stable—that is, the compound is easily decomposed. By passing it through a hot tube it is partially decomposed into hydrogen and sulphur. The action is reversible, for by passing hydrogen and sulphur vapour through a hot porcelain tube hydrogen sulphide is formed.

Chlorine will decompose hydrogen sulphide, resulting in the formation of hydrochloric acid and sulphur.

White paint—basic lead carbonate—is blackened by hydrogen sulphide, owing to the formation of lead sulphide.

The salts of hydrogen sulphide (sulphides) are readily decomposed by acids.

Extended Use of the Term Reduction.

So far a reducing agent has been considered as one which will remove oxygen from a compound. The term is also applied to substances which will—

(i) decrease the non-metallic portion of a compound; or
(ii) add hydrogen to an element or a compound.

Hydrogen sulphide will bring about the changes just mentioned, and therefore is a reducing agent. For example:

(i) It will remove oxygen from sulphuric acid.

$$\text{hydrogen sulphide} + \text{sulphuric acid} \Big\} \text{form} \Big\{ \text{sulphurous acid} + \text{sulphur.}$$
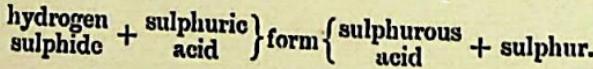
(ii) It will decrease the non-metallic portion of ferric[1] chloride.

$$\text{hydrogen sulphide} + \text{ferric chloride} \Big\} \text{form} \Big\{ \text{ferrous chloride} + \text{hydrochloric acid} + \text{sulphur.}$$
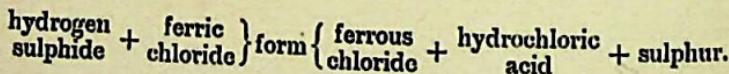
(iii) It will combine hydrogen and chlorine.

$$\text{hydrogen sulphide} + \text{chlorine} \Big\} \text{form} \Big\{ \text{hydrochloric acid} + \text{sulphur.}$$

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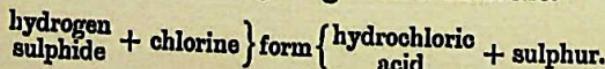
[1] There are two *iron chlorides*. The one with the greater percentage of chlorine in it is called *ferric chloride*, and the other is called *ferrous chloride*.

Use of Hydrogen Sulphide in Analytical Chemistry.

The sulphides of manganese, iron, and zinc are readily decomposed by hydrochloric acid. Those of copper, silver, and mercury are not so decomposed. A separation of these metals can therefore be effected by passing hydrogen sulphide through a solution of the salts of these metals in hydrochloric acid.

The sulphides of copper, silver, mercury (and others), will be precipitated, for they are insoluble in hydrochloric acid. The sulphides of iron, zinc (and others), will not be precipitated, for they are soluble in hydrochloric acid.

Some sulphides also have conspicuous colours, which serve to distinguish the metal present. Zinc sulphide is white, cadmium sulphide is yellow, mercury sulphide is black.

Composition of Hydrogen Sulphide.—*Analysis.*—On burning hydrogen sulphide in a limited supply of air, sulphur is deposited. This shows that *the gas contains sulphur*.

To show that it also contains hydrogen, the hydrogen may be oxidized to water by means of a metallic oxide as follows.

Experiment 93.—To oxidize the hydrogen in hydrogen sulphide into water.

Hydrogen sulphide is generated from hydrochloric acid and iron sulphide. It is dried by passing it over phosphorus pentoxide and then passed over heated mercuric oxide. The water produced may be collected by conducting the gases into a well-cooled receiver.

The fact that hydrogen sulphide contains its own volume of hydrogen may be illustrated by means of the apparatus shown in fig. 76. The tube T contains at S a small quantity of tin. The tube is filled with hydrogen sulphide collected over mercury. The tin is then heated, and combines with the sulphur of the hydrogen sulphide, setting free the hydrogen. When the whole of the gas has been decomposed in this way, the volume of hydrogen liberated is seen to be equal to the volume of hydrogen sulphide employed.

Synthesis.—Hydrogen sulphide may be synthesized from

its elements by passing sulphur vapour and hydrogen through a hot porcelain tube.

Distribution.—Hydrogen sulphide is found amongst the gases given out by volcanoes, in some mineral waters, and whenever animal or vegetable matter containing sulphur is decaying.

SULPHUR DIOXIDE

It has already been seen that when sulphur burns in air or oxygen, sulphur dioxide is produced. Similarly, in extracting iron and copper from pyrites (metallic sulphides), on roasting the ore, the sulphur oxidizes to sulphur dioxide and the metal oxidizes also.

Action of some Elements upon Hot Concentrated Sulphuric Acid.

Experiment 94.—Cautiously warm a little concentrated sulphuric acid in a test-tube with (*a*) iron, (*b*) zinc, (*c*) carbon, (*d*) sulphur, (*e*) copper, (*f*) mercury in turn. Identify the gas given off in each case. Which of these elements liberate sulphur dioxide from sulphuric acid? It is possible to name two of the elements present in sulphuric acid from the results of this experiment. What elements are they?

In the laboratory sulphur dioxide is usually made by reducing sulphuric acid by means of copper.

Experiment 95.—To prepare sulphur dioxide and to examine its properties.

(i) Use the apparatus shown in fig. 63. Place some copper turnings in the flask and pour in sufficient concentrated sulphuric acid to cover the lower end of the thistle funnel. Heat the flask containing the copper and sulphuric acid on a sand-bath. Collect the gas by downward displacement.

(ii) Examine the gas according to the usual scheme (p. 46). Also perform the following experiments with the gas:—

(*a*) Wet some coloured leaves and place them in a jar of the gas. Is the gas a bleaching agent?

(*b*) Remove the delivery-tube from the apparatus (fig. 64), and replace it by the apparatus shown in fig. 84.

A· is a U-tube immersed in a freezing-mixture of ice and salt. P is a 25-cu.-cm. pipette which reaches to the bottom of the test-tube T, which contains 20 cu. cm. of sodium carbonate solution.

Heat the copper and sulphuric acid, and most of the sulphur · dioxide generated will be condensed to a liquid in A. Any
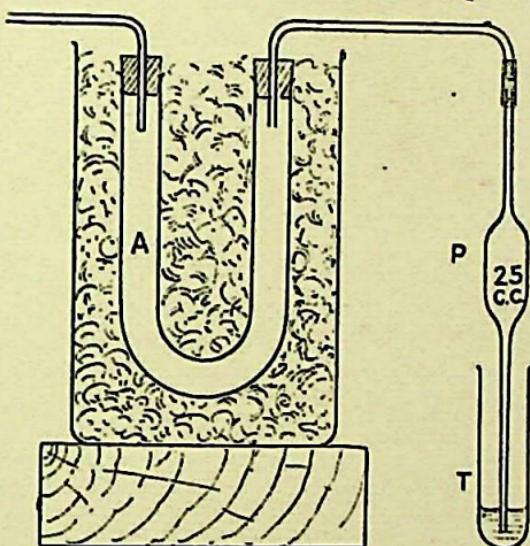
Fig. 84.—Preparation of Liquid Sulphur Dioxide

sulphur dioxide not condensed in A will be absorbed by the sodium carbonate in T. The pipette P will prevent the sodium carbonate in T from rushing over into A if the evolution of sulphur dioxide ceases. Examine the liquid sulphur dioxide collected in A. Notice how rapidly it evaporates and how cold it remains even when removed from the freezing-mixture. Add a few drops of hydrochloric acid to the solution in T. Can you identify the gas given off?

(*c*) Pass some sulphur dioxide through some chlorine water by placing the end of the delivery-tube (fig. 64) in some chlorine water contained in a test-tube. Test the solution for hydrochloric acid (see p. 124).

(*d*) Dip a piece of filter-paper in some potassium dichromate solution. Hold the yellow paper in some sulphur dioxide. What effect has sulphur dioxide on the colour of the potassium dichromate?

(*e*) Pass some sulphur dioxide through a solution of potassium permanganate. What effect has sulphur dioxide on the colour of the permanganate?

Potassium dichromate and potassium permanganate are two compounds containing a large quantity of oxygen, which they readily part with to reducing agents. When potassium dichromate is reduced the colour changes to green; when potassium permanganate is reduced the solution becomes either colourless or brown.

Properties of Sulphur Dioxide.—Sulphur dioxide is a colourless heavy gas with a suffocating smell. It will not burn nor support combustion. The gas is very soluble in water, forming sulphurous acid. Sulphur dioxide can be entirely expelled from the solution by boiling.

The salts of sulphurous acid are called sulphites. Sulphur dioxide is absorbed by caustic soda forming sodium sulphite. If excess of sulphur dioxide is passed through the solution the acid sulphite or bisulphite of soda is formed. Compare this reaction with the effect of carbon dioxide on caustic soda and on lime-water.

$$\left.\begin{array}{c}\text{calcium}\\ \text{hydroxide}\end{array} + \begin{array}{c}\text{carbon}\\ \text{dioxide}\end{array}\right\} \text{form} \left\{\begin{array}{c}\text{calcium}\\ \text{carbonate}\end{array} + \text{water}\right.$$

$$\left.\begin{array}{c}\text{calcium}\\ \text{carbonate}\end{array} + \text{water} + \begin{array}{c}\text{calcium}\\ \text{hydroxide}\end{array}\right\} \text{form} \left\{\begin{array}{c}\text{calcium}\\ \text{bicarbonate.}\end{array}\right.$$

$$\left.\begin{array}{c}\text{sodium}\\ \text{hydroxide}\end{array} + \begin{array}{c}\text{carbon}\\ \text{dioxide}\end{array}\right\} \text{form} \left\{\begin{array}{c}\text{sodium}\\ \text{carbonate}\end{array} + \text{water}\right.$$

$$\left.\begin{array}{c}\text{sodium}\\ \text{carbonate}\end{array} + \text{water} + \begin{array}{c}\text{sodium}\\ \text{hydroxide}\end{array}\right\} \text{form} \left\{\begin{array}{c}\text{sodium}\\ \text{bicarbonate.}\end{array}\right.$$

$$\left.\begin{array}{c}\text{sodium}\\ \text{hydroxide}\end{array} + \begin{array}{c}\text{sulphur}\\ \text{dioxide}\end{array}\right\} \text{form} \left\{\begin{array}{c}\text{sodium}\\ \text{sulphite}\end{array} + \text{water}\right.$$

$$\left.\begin{array}{c}\text{sodium}\\ \text{sulphite}\end{array} + \text{water} + \begin{array}{c}\text{sodium}\\ \text{hydroxide}\end{array}\right\} \text{form} \left\{\begin{array}{c}\text{sodium}\\ \text{bisulphite.}\end{array}\right.$$

When sulphur dioxide is passed into sodium carbonate, sodium bisulphite is formed. This is one method of placing sulphur dioxide on the market. The sulphur dioxide is

liberated from the sulphite on treatment with sulphuric acid.
Sulphur dioxide is sometimes prepared in the laboratory by
this method. Concentrated sulphuric acid is dropped by means
of a dropping-funnel into a solution of sodium bisulphite con-
tained in a flask.

Sulphur dioxide is detrimental to vegetable life. Vegeta-
tion near works where sulphur dioxide is set free is killed by
the action of the gas. Even the small amount of sulphur
dioxide in the air of towns is injurious to plant life. Advan-
tage is taken of this effect of sulphur dioxide to prevent the
growth of moulds (lowly plants) in casks for wine or beer,
which are fumigated by means of sulphur dioxide.

Sulphur dioxide bleaches organic colouring-matter. For
bleaching silk or wool it is preferable to chlorine, which
renders the fibres of these substances hard and brittle. Sul-
phur dioxide bleaches by uniting with oxygen to form sul-
phuric acid. Contrast this with chlorine, which bleaches by
uniting with hydrogen to form hydrochloric acid (p. 132).
The colour of articles bleached by means of sulphur dioxide is
often restored by acids or alkalis. This explains why straw
hats become yellow if washed with soap which contains an
alkali.

A solution of sulphur dioxide rapidly absorbs oxygen and
becomes sulphuric acid. For example, it will withdraw the
oxygen from potassium permanganate and potassium dichro-
mate. It also reduces chlorine to hydrochloric acid.

$$\left.\begin{array}{l}\text{sulphurous} \\ \text{acid}\end{array} + \text{chlorine} + \text{water}\right\} \text{form} \left\{\begin{array}{l}\text{sulphuric} \\ \text{acid}\end{array} + \begin{array}{l}\text{hydrochloric} \\ \text{acid.}\end{array}\right.$$
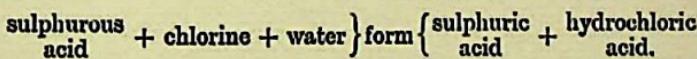
Hence sulphur dioxide is a reducing agent (see p. 166). For
this reason it is employed under the name of antichlor to
remove the last traces of chlorine from articles after bleaching.
The sulphuric and hydrochloric acids produced (see above)
are washed out of the fabric.

Sulphur dioxide is easily liquefied at atmospheric pressure
by cooling it by means of a freezing-mixture of ice and salt.
Liquid sulphur dioxide is used as a refrigerating agent.

Composition of Sulphur Dioxide. (*Synthesis.*) Sulphur di-
oxide can be synthesized from the elements sulphur and
oxygen, as in Experiment 35 (iii).

By means of the apparatus shown in fig. 85 it may be
shown that sulphur dioxide contains
its own volume of oxygen.

A piece of sulphur S is supported
on the platinum spiral A. (Platinum
is not attacked by sulphur.) The wires
W are connected to an electric battery.
The tube T, which must be dry, is then
partly filled with oxygen. The re-
mainder of the tube T and part of R is
filled with mercury. The volume of
oxygen is noted. An electric current
is then passed through the coil A,
which becomes red-hot if the current
is strong enough. The sulphur then
burns and forms sulphur dioxide. The
heat produced causes the sulphur di-
oxide to expand. When the gas has
cooled to the original temperature it is
seen that the volume of sulphur dioxide
produced is almost exactly equal to
the volume of oxygen employed.
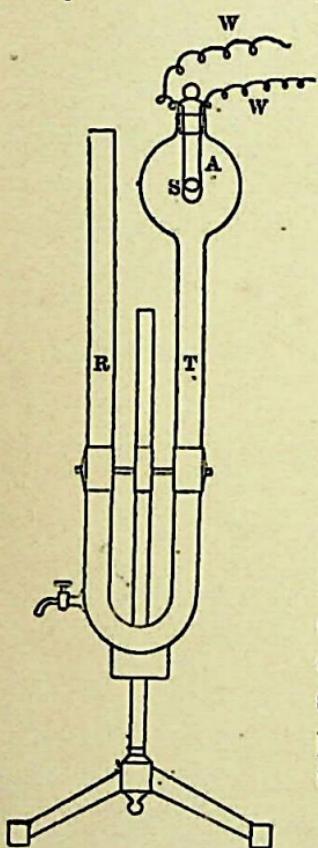
Fig. 85.—Composition of
Sulphur Dioxide

SULPHUR TRIOXIDE

When sulphur burns in oxygen the
oxide formed is mainly sulphur dioxide; but a little sulphur
trioxide—a higher oxide of sulphur—forms at the same time.
This accounts for the fact that in the experiment just
described, the volume of sulphur dioxide is rather less than
the volume of oxygen.

It is impossible to make sulphur dioxide and oxygen com-
bine by heat alone. Combination can be brought about by
heating the two gases in contact with finely divided platinum.

Experiment 96.--To prepare sulphur trioxide.

The apparatus used is shown in fig. 86. A is a flask containing potassium chlorate, from which the oxygen is generated. B contains sulphuric acid and copper, to yield the sulphur dioxide. C is a wash-bottle containing concentrated sulphuric acid. D is a bulb-tube containing platinized asbestos (asbestos fibre coated with finely divided platinum).

The flasks A and B and the bulb D are heated.

In passing over the heated platinized asbestos the oxygen and sulphur dioxide combine and form sulphur trioxide, which issues from E as a dense cloud.

To collect the gas, an absolutely dry receiver, say a U-tube,
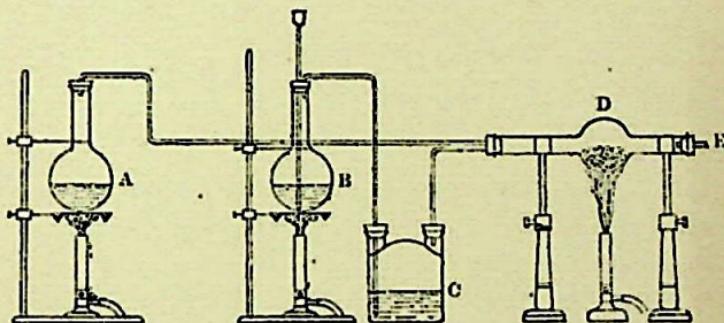
Fig. 86.—Preparation of Sulphur Trioxide

kept cool by ice-cold water, should be attached to E, and another U-tube, standing in a freezing-mixture, connected in turn to the first. A delivery-tube connected to the outlet of this second U-tube should be arranged to dip into a beaker of caustic soda to absorb any sulphur dioxide not condensed (see fig. 84).

Properties.—Sulphur trioxide is a colourless liquid which boils at 46° C., and solidifies to white silky needle-like crystals at 15° C. It forms dense white fumes in moist air, and when it is dropped on water a hissing noise is heard. In both cases the sulphur trioxide combines with water to form sulphuric acid. Thus sulphur trioxide is the anhydride (see p. 51) of sulphuric acid, just as sulphur dioxide is the anhydride of sulphurous acid.

Sulphuric trioxide is sold, dissolved in sulphuric acid, as fuming or Nordhausen sulphuric acid. This acid on distilling yields sulphur trioxide. Sulphur trioxide can also be obtained by distilling sulphuric acid with phosphorus pentoxide. The phosphorus pentoxide abstracts the elements of water from the sulphuric acid and leaves the anhydride, which distils over into the receiver. (This method of preparation is not suitable for the laboratory, owing to the dangerous nature of the mixture.)

SULPHURIC ACID

Experiment 97.—To illustrate the manufacture of sulphuric acid.
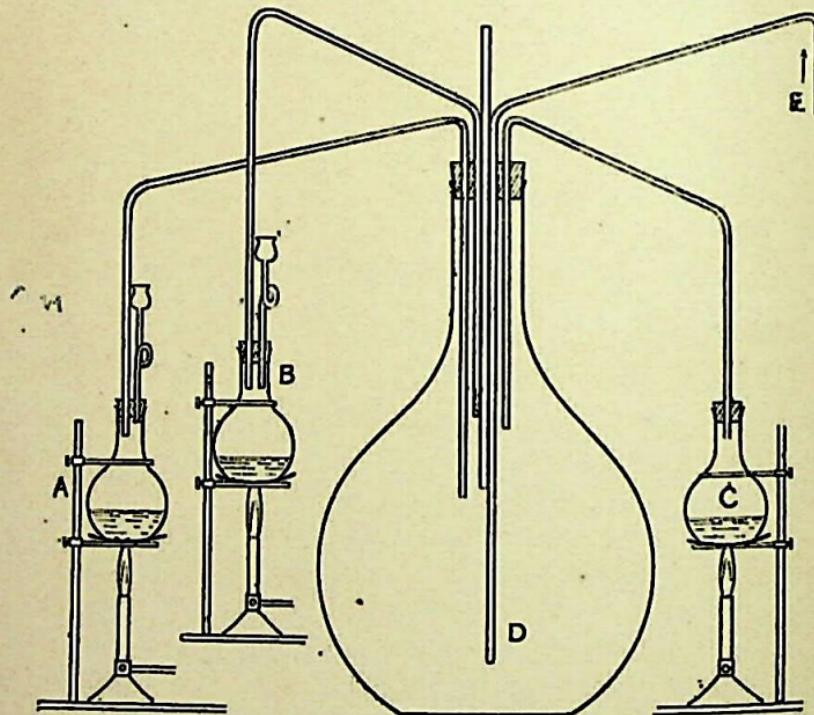
Fig. 87.—Preparation of Sulphuric Acid

Fit up the apparatus shown in fig. 87.

D is a large flask of (say) 5 litres capacity, provided with a stopper pierced with five holes. Through three of these holes

delivery-tubes pass into the small flasks A B C. One delivery-tube, E, is connected to a compression-pump so that air may be pumped into D. Through the remaining hole in the stopper of D an exit-pipe passes. This tube reaches nearly to the bottom of D.

A contains nitric acid.

B contains copper and concentrated sulphuric acid (see p. 168).

C contains water.

Boil the nitric acid in A slowly, and gently heat the copper and sulphuric acid in B. The flask D will then contain oxygen (air), sulphur dioxide, and nitric acid vapour. The nitric acid will oxidize the sulphur dioxide into sulphuric acid, being itself reduced to nitrogen peroxide.

$$\underset{\text{nitric acid}}{H\,NO_3} + \left.\underset{\substack{\text{sulphur}\\\text{dioxide}}}{SO_2}\right\} \text{form} \left\{\underset{\text{acid}}{\overset{HSO_4}{\text{sulphuric}}} + \underset{\text{peroxide.}}{\overset{NO}{\text{nitrogen}}}\right.$$
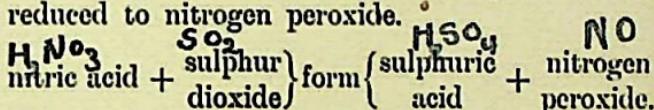
The formation of reddish-brown vapour in D indicates the production of nitrogen peroxide. The sulphur dioxide and moisture present in D then unite to form sulphurous acid, which is oxidized by the nitrogen peroxide into sulphuric acid.

$$\underset{\text{peroxide}}{\overset{NO}{\text{nitrogen}}} + \underset{\text{water}}{\overset{H_2O}{}} + \underset{\substack{\text{sulphur}\\\text{dioxide}}}{\overset{SO_2}{}} \left.\right\} \text{form} \left\{\underset{\text{acid}}{\overset{H_2S_2}{\text{sulphuric}}} + \underset{\text{oxide.}}{\overset{NO}{\text{nitric}}}\right.$$
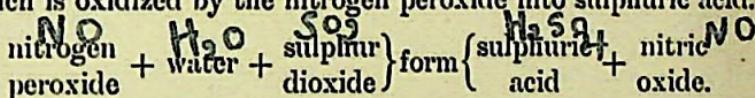
The reaction just described takes place in two stages. With an insufficient quantity of water present in D the nitrogen peroxide, water, and sulphur dioxide form a crystalline compound (nitro-sulphuric acid). The appearance of large white crystals on the sides of D indicates this stage in the reaction.

When these crystals appear, boil the water in C. This will provide sufficient moisture in D to decompose the crystals, with the formation of sulphuric acid and nitric oxide. If there is sufficient oxygen in D the nitric oxide set free will form red nitrogen peroxide. If not, air must be pumped in through E. Provided that air and steam are passed into D as required, the process is continuous.

The nitrogen peroxide oxidizes a further quantity of sul-

phur dioxide in the presence of water to sulphuric acid, being itself reduced again to nitric oxide. The nitric oxide is oxidized by the air present to nitrogen peroxide, and so on.
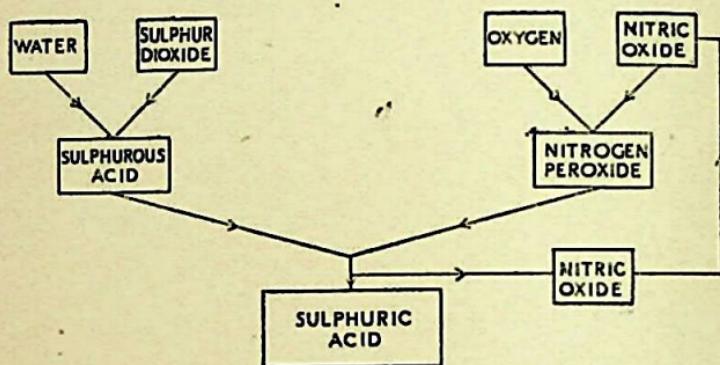
Preparation.—Sulphuric acid may be formed by dissolving its anhydride (sulphur trioxide) in water. It is also obtained by the oxidation of sulphurous acid. This oxidation proceeds slowly when sulphurous acid is exposed to the air. It takes place instantly when such oxidizing agents as nitric acid or nitrogen peroxide are present. The method employed in Experiment 97 is an illustration of the commercial method of manufacturing sulphuric acid.

Manufacture.—The sulphur dioxide is obtained by roasting iron pyrites (sulphide of iron) in the kiln κ (fig. 88). The sulphur in the pyrites burns to form sulphur dioxide, which, with air, passes into rectangular chambers lined with lead, L.C.

On its way, the sulphur dioxide passes over pots containing potassium nitrate and sulphuric acid (nitre pots, N.P.). The hot sulphur dioxide vaporizes the nitric acid formed in the nitre pots and carries the vapour along with it into the leaden chambers. Here the nitric acid, air, and sulphur dioxide are mixed with steam generated in the steam boiler, S.B.).

The sulphuric acid (formed as described in Experiment 97) collects on the floor of the leaden chambers. The unused gases in L.C. then consist mainly of nitrogen and oxides of

nitrogen. To collect the latter the gases are made to pass through the Gay Lussac Tower, G L T., before escaping. This tower is filled with coke down which a stream of concentrated sulphuric acid flows. The sulphuric acid dissolves the oxides of nitrogen. This impure sulphuric acid is then pumped to the top of the Glover Tower, G T. The Glover Tower is filled with flints, and the impure acid and a stream of water are allowed to run down the flints. The impure sulphuric acid, on being diluted by the water, gives up the oxides of nitrogen it contained, and they are swept into the leaden chambers by the sulphur dioxide from K. At the same time the hot gases from K again concentrate the sulphuric acid in the Glover Tower, and carry the moisture thus obtained into the leaden

Fig. 88.—Diagram of the Sulphuric Acid Manufacture

K, Pyrites kiln. N P, Nitre pots. G T, Glover tower. L C, Lead chambers. G L T, Gay Lussac tower. S B, Steam boiler.

chambers. Under these circumstances very little nitric acid from the nitre pots is needed.

The acid which collects in the leaden chambers contains about 29 per cent of water. This acid may be run off into leaden pans, and concentrated by boiling until it contains 18 per cent of water. Further concentration in these pans would cause the acid to attack the lead. It may be concentrated until it contains only 2 per cent of water (oil of vitriol) by distilling it in glass or platinum stills.

Properties.—Sulphuric acid is a colourless oily liquid. The .density of the pure acid is 1·85. Sulphuric acid has a very great affinity for water (see Experiment 98 and page 190). When the acid is added to water a large amount of heat is generated (see p. 82). At the same time the volume of the mixture is diminished. Sulphuric acid will dissolve sulphur trioxide, forming "fuming" or Nordhausen sulphuric acid. Fuming sulphuric acid is manufactured by distilling iron sulphate (see p. 299).

Experiment 98.—Dehydrating effect of sulphuric acid.

(i) Warm a piece of wood with a little concentrated sulphuric acid in a test-tube. Notice the charring which takes place, due to the abstraction of water from the wood.

(ii) Add a little concentrated sulphuric acid to a strong solution of sugar in a beaker. [Sugar is a compound of carbon, hydrogen, and oxygen.]

(iii) Expose a known weight of concentrated sulphuric acid in a watch-glass to the air for ten minutes. Re-weigh the watch-glass and its contents, and notice the increase in weight.

QUESTIONS ON CHAPTER XV

1. How is sulphur dioxide prepared? What chemical changes take place when sulphur dioxide is passed into (a) chlorine water, (b) nitric acid? (C. L.)

2. How would you bring about the combination of (a) hydrogen and oxygen, (b) hydrogen and sulphur? Give some account of the compound produced in each case. (C. L.)

3. How is sulphuretted hydrogen prepared? Why is it

called a reducing agent? What chemical changes take place when sulphuretted hydrogen is passed into a solution of (*a*) copper sulphate, (*b*) sulphur dioxide? (C. L.)

4. Describe a method for preparing sulphur trioxide. Write an account of the chemical and physical properties of this substance. (C. L.)

5. Describe the chemical changes which take place when (*a*) sodium, (*b*) sulphur, (*c*) sulphuretted hydrogen, (*d*) iron, are burned in oxygen. (C. L.)

6. How is sulphur dioxide prepared? Describe experiments to illustrate its character as a reducing agent? (C. L.)

7. How would you prepare sulphuretted hydrogen? What happens when sulphuretted hydrogen is passed into (*a*) chlorine water, (*b*) nitric acid, (*c*) ferric sulphate? (C. L.)

8. How are sulphuric and sulphurous acids prepared? What salts could you obtain by allowing these acids to react with caustic soda? (O. L.)

9. What do you mean by an allotropic form? Briefly describe the allotropic forms of sulphur.

10. Describe the preparation and properties of hydrogen sulphide. How could you most readily obtain samples of hydrogen and of sulphur from sulphuretted hydrogen? (O. L.)

CHAPTER XVI

CARBON

I. Charcoal.

Experiment 99.—To prepare wood charcoal.

Cut several small pieces of wood of equal size. Place a few of them in a clay crucible and cover them with a layer of sand to exclude the air. Heat the crucible strongly, and try to ignite the fumes which rise from the contents.

When fumes are no longer given off, stop the heating, and when the crucible is cold examine the charcoal in it. Compare the size of these pieces with that of the pieces of wood which

were not heated. Notice that the charcoal exhibits the structure of the wood, and that it is much smaller than the wood from which it was made.

Experiment 100.—To find the effect of heat upon charcoal.

Heat a piece of charcoal on a spoon to allow free access of the air. Continue the heating until only a whitish powder is left. This is the *ash*. It consists of various mineral substances absorbed from the soil by the tree from which the wood was obtained.
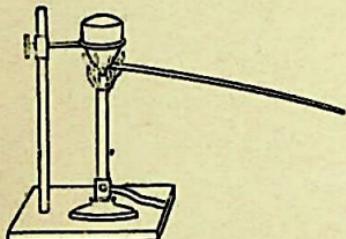
Fig. 89.—Production of Coke from Coal

Experiment 101. — To prepare various forms of charcoal from organic substances and to examine their properties.

Repeat Experiment 99 without attempting to determine the change in size, and Experiment 100, using pieces of (i) coal, (ii) bone, (iii) sugar. The powdered coal may be heated in the bowl of a clay-pipe which has been closed at the top by means of moist clay (fig. 89). The coal-gas which issues from the pipe-stem may then be lighted. Find whether the charcoal obtained will sink or float in water. The charcoal had better be powdered and wetted before testing.
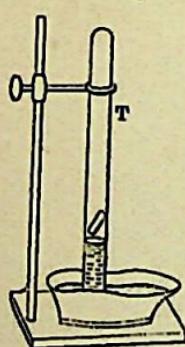
Fig. 90.—Absorption of Gas by Charcoal

Experiment 102.—To illustrate the absorption of gases by charcoal.

Partly fill the glass tube T (fig. 90) with carbon dioxide or ammonia gas collected over mercury. Pass a piece of freshly heated charcoal under the tube. The charcoal will float to the top of the mercury. Mark the height of the mercury in the tube. Allow the apparatus to stand for a few days. It will then be noticed that the mercury has risen in the tube to take the place of the gas absorbed by the charcoal.

Wood if heated without free access of air gives off inflammable gases. These are mainly hydrogen and compounds of hydrogen and carbon. The residue consists of a black substance called charcoal. When this charcoal is burnt in air it forms carbon dioxide, and leaves a small quantity of ash.

Hydrochloric or sulphuric acid will dissolve the ash, but neither has any effect on the charcoal.

Neglecting the ash, chemists find it impossible to decompose the charcoal. Hence charcoal is regarded as an element. It is one form of the element carbon.

Sugar charcoal, bone charcoal, lamp-black (soot), coal, coke, and gas carbon are other varieties of charcoal which consist of more or less pure carbon.

Lamp-black is formed when compounds of hydrogen and carbon burn in an insufficient supply of air. The hydrogen in the compound burns to water. The carbon is deposited as soot. Some hydrogen always remains in the carbon (see Experiment 102). It can be removed by heating the lamp-black in a current of chlorine.

$$\text{carbon} + \text{hydrogen} + \text{chlorine form} \begin{cases} \text{hydrochloric} \\ \text{acid} \end{cases} + \text{carbon.}$$
$$C \qquad\quad H \qquad\qquad Cl \qquad\qquad\quad HCl \qquad\quad C$$
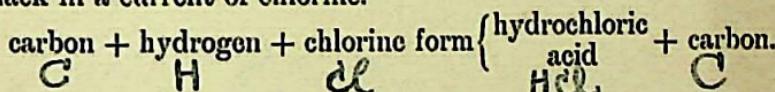
Lamp-black is used in making printer's ink (see p. 131), black paint, and boot polishes.

Coal.—All plants contain, amongst other elements, carbon, oxygen, hydrogen, nitrogen, and sulphur. When plants decay in the absence of air, compounds of carbon and oxygen (carbon dioxide) and carbon and hydrogen (marsh gas) are given off. The residue is coal, an impure form of carbon. Peat and lignite are stages in the formation of coal from decaying plants.

Coal is therefore fossil charcoal. It is formed in a similar manner to wood charcoal. The main difference in the formation is that the temperature during the formation of coal is lower than the temperature of formation in the case of wood charcoal. Hence some hydrogen remains in the coal.

Analyses of samples of coal are given below:—

	Carbon.	Hydro-gen.	Oxygen.	Nitro-gen.	Sul-phur.	Ash.
Northumberland (England)	78·7	6	10	2·4	1·5	1·4
South Wales ...	92·6	3·3	2·5	—	—	1·6

Coke —Coke is formed when coal is heated with exclusion of the air. During the formation some of the hydrogen in
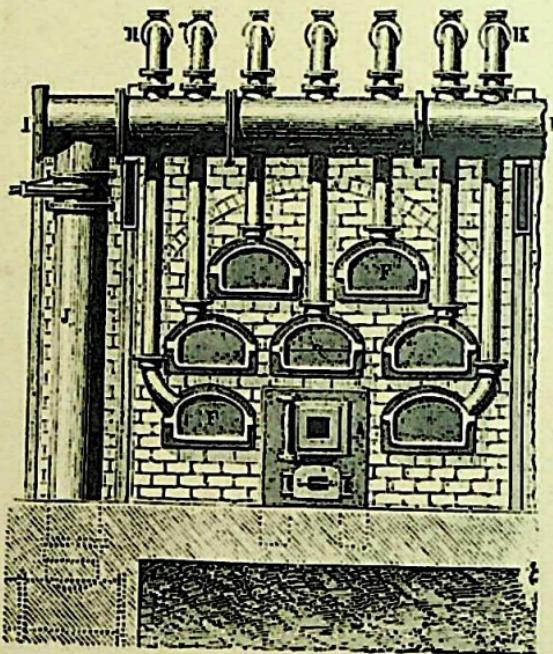
Fig. 91.—Group of Gas Retorts

A, Furnace. FF, Retorts. HH, Ascension pipes conveying gas to (II) the hydraulic main. J, Pipe through which gas passes to the condensers.

the coal combines with some of the carbon, and they form compounds of carbon and hydrogen.

Some of the hydrogen combines with the nitrogen in the coal and forms ammonia. Some hydrogen is liberated un-combined. The residue (coke) contains about 90 per cent of

carbon. The gases given off are used for illuminating and heating purposes (coal-gas) after being purified.

In the manufacture of coal-gas, coal is heated in retorts (fig. 91), and the coke remains in the retorts. Some of the carbon from the coal forms a hard deposit on the retorts. This is very hard and fairly pure carbon. It is used, under the name of *gas carbon*, for making carbon rods for electric arc lamps and for electric batteries.

Wood charcoal is prepared on a large scale by heating branches of small trees. Where wood is plentiful the branches are piled in a heap and covered with clay and earth. The
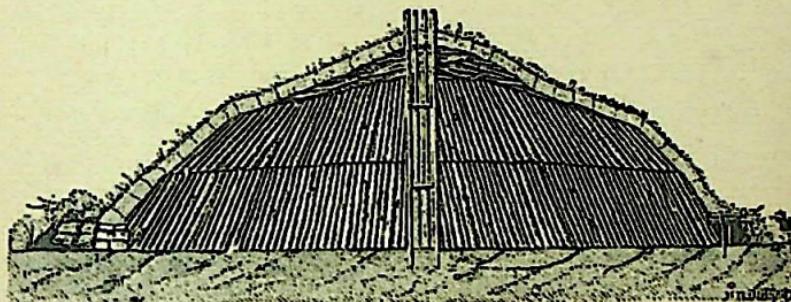
Fig. 92.—Preparation of Wood Charcoal

pile is then set on fire (fig. 92). This method is very wasteful, both as regards the carbon and also as regards the volatile substances which escape into the air. A more economical method is to heat the wood in retorts and condense the volatile liquids given off.

Properties of Wood Charcoal.—Charcoal is a black substance of low density ($1\frac{1}{2}$–2). Wood charcoal floats on water, owing to the fact that it is porous. The air in the pores buoys up the charcoal.

Wood charcoal readily combines with oxygen and forms carbon dioxide. Charcoal is a bad conductor of heat and of electricity.

These properties, however, vary in different kinds of charcoal. The variation is caused by the different temperatures at which the carbonization takes place. Gas carbon, for

example, only burns with difficulty, and is a much better conductor of heat than wood charcoal.

It is very difficult to change charcoal from the solid state. In the electric arc, however, charcoal is changed into a vapour at about 3500° C.

Charcoal is insoluble in almost every solvent. Molten iron will, however, dissolve it. From a solution in iron, charcoal is deposited in a crystalline form known as *graphite*.

Charcoal readily absorbs quantities of gases into its pores. For example: 1 cu. cm. of carbon will absorb 17 cu. cm. of oxygen, or 67 cu. cm. of carbon dioxide, or 171 cu. cm. of ammonia.

The insides of sewer ventilators are often packed with charcoal in order to prevent noxious gases from escaping into the air. Charcoal is able to render colourless (decolorize) many coloured solutions. It is used for this purpose in sugar refining. The brown sugar is decolorized by means of animal charcoal.

Carbon has a great affinity for oxygen, and, in consequence, it is a powerful reducing agent. It is used in extracting the metals iron, copper, lead, zinc, &c., from their ores.

iron oxide + carbon form iron + carbon dioxide.
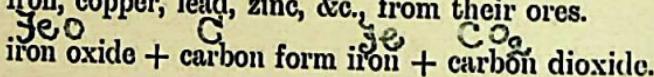
The carbon dioxide is then reduced by the carbon, as explained on p. 188.

II. **Graphite.**—Grey cast iron contains a small amount of carbon in the form known as graphite (see p. 295).

Experiment 103.—To obtain graphite from iron.
Dissolve some iron filings in dilute sulphuric acid. Filter and wash the residue with water. The iron dissolves in the acid, forming iron sulphate (ferrous sulphate). The ferrous sulphate dissolves in the water. The graphite is unacted upon by the acid and remains on the filter-paper.

Properties of Graphite.—Graphite is also called plumbago and black-lead, although it contains no lead, but only carbon.

It occurs naturally in the form of dark-grey masses, which

have a lustre (shine) rather like the lustre possessed by most metals. It is found in Ceylon, India, Bohemia, Bavaria, Siberia, California, and other places.

Graphite can be prepared artificially by dissolving charcoal in molten iron and allowing the solution to cool.

Graphite differs from charcoal in several respects. The density of graphite is nearly twice that of charcoal. Graphite is a fairly good conductor of heat and of electricity. It burns only with great difficulty, forming carbon dioxide; it is much softer than charcoal and will mark paper. For this reason it is used in the manufacture of pencils and also as a lubricant instead of oil. It is also used under the name of "black-lead" to polish ironwork.

Like charcoal, graphite cannot be melted, but is volatilized at very high temperatures. It is not attacked by chlorine, nor even by fused potassium hydroxide, two very active reagents.

Mixed with potassium chlorate and heated, graphite burns and forms carbon dioxide. This is the most convenient method of oxidizing the substance. A mixture of potassium dichromate and sulphuric acid—a powerful oxidizing agent—brings about a similar oxidation. Nitric acid and potassium chlorate together oxidize graphite to a white solid called graphitic acid. This test serves to distinguish graphite from charcoal and diamond, neither of which form graphitic acid.

III. Diamond. — Another crystalline form of carbon which occurs naturally is the diamond (fig. 93). Pure diamond is a colourless, transparent substance. It is, however, often found as coloured crystals, the colour being due to traces of foreign metals.

Fig. 93.—Crystals of Diamond

Diamond is brittle and infusible. It is the hardest of all
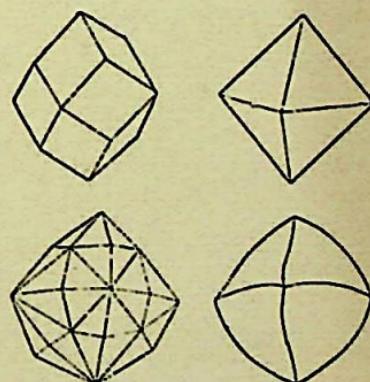
substances and is therefore used for glass-cutting, for boring, and for grinding and polishing hard substances. The density of diamond is about $3\frac{1}{2}$.

Diamond is insoluble in all liquids. It can be oxidized to carbon dioxide by heating very strongly in oxygen or by means of potassium dichromate and sulphuric acid at 200° C.

Diamonds are found in South Africa, Brazil, India, the Ural Mountains, Borneo, and Australia.

Small diamonds have been artificially prepared by the French chemist, Moissan. He packed charcoal in an iron cylinder, which he placed in molten iron at a very high temperature. The molten iron in which the charcoal became dissolved was then quickly cooled. The outside of the molten iron contracted on solidifying, and exerted a great pressure on the still molten iron inside. The carbon was thus subjected to a high temperature at great pressure.

On dissolving the iron in acid, small crystals of diamond were obtained.

Comparison of the Three Forms of Carbon.

	Density.	Hardness.	Readiness with which it combines with Oxygen.	Conductor of Heat and Electricity.
Charcoal ...	1·5-2	soft	fairly readily	bad.
Graphite ...	2·5	soft	with difficulty	good.
Diamond ...	3·5	hardest known substance	with difficulty	bad.

Combustion of Charcoal, Graphite, and Diamond.

Experiment 104.—To find the volume of carbon dioxide obtained by burning carbon in oxygen.

The apparatus shown in fig. 85 may be used.

A piece of pure charcoal is placed on the platinum spiral A, which is connected by wires to an electric battery. The bulb and the tube T are partly filled with oxygen. The oxygen

is confined by mercury, which fills the bend of the tube. The mercury being adjusted so that it stands at the same level in both limbs, the volume of oxygen is noted.

The platinum spiral is made red-hot by passing a current of electricity through the wire. The carbon burns and forms carbon dioxide. The heat generated causes the gases to expand, but when they have cooled to the original temperature it will be seen that *the volume of carbon dioxide produced is equal to the volume of oxygen used.*

Experiment 105.—To find the weight of carbon dioxide obtained from a known weight of carbon.
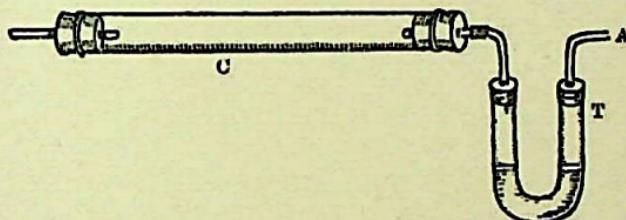
Fig. 94.—Weight of Carbon Dioxide from a known Weight of Carbon

A piece of pure graphite is weighed and placed in a porcelain boat in a combustion-tube c (fig. 94). The combustion-tube is connected at one end to an apparatus for supplying pure, dry oxygen. At the other end it is connected to *weighed* absorption-tubes T, containing caustic soda.

The graphite is heated to redness by means of a Bunsen burner and a stream of oxygen passed over it by attaching the outlet-tube A to an aspirator. The graphite burns to carbon dioxide, which is absorbed by the caustic soda.

$$CO_2 \begin{matrix} \text{carbon} \\ \text{dioxide} \end{matrix} + \begin{Bmatrix} \text{sodium} \\ \text{hydroxide} \end{Bmatrix} \text{ form } \begin{Bmatrix} \text{sodium} \\ \text{carbonate} \end{Bmatrix} + \text{water.}$$
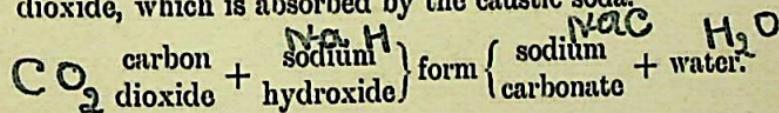
The increase in weight of the tubes containing caustic soda gives the weight of the carbon dioxide produced. The decrease in weight of the porcelain boat gives the weight of carbon oxidized. The porcelain boat will contain a little ash at the close of the experiment.

The results of careful experiments show that 1 *grm. of graphite on burning yields* 3·66 *grm. of carbon dioxide.*

Charcoal, Graphite, and Diamond are Allotropic Forms of the Element Carbon.

Experiments 104 and 105 have been performed, using (1) charcoal, (2) graphite, (3) diamond. In each case it has been found that equal masses of these three substances yield exactly the same volume (and weight) of carbon dioxide if the substances are pure.

This shows that notwithstanding the differences in appearance and properties of these three substances *they are only different forms of one and the same element.* They are therefore called allotropes or allotropic forms of carbon (see p. 161).

CARBON MONOXIDE

We have already discussed one oxide of carbon—carbon dioxide (see Chapter IX).

Carbon under certain conditions forms another oxide called carbon monoxide. *This is a very poisonous gas, and great care must be exercised in its preparation. On no account must it be allowed to escape needlessly into the air of the laboratory.*

Experiment 106.—To prepare carbon monoxide by the reduction of carbon dioxide, and to examine its properties.

The flask F (fig. 95), which contains pieces of marble, is connected to the combustion-furnace (fig. 96). The iron tube T T of the combustion-furnace is loosely filled with pieces of charcoal. The outlet-tube from C dips into a strong solution of caustic soda contained in the bottle B (fig. 95). The caustic soda will absorb any carbon dioxide not reduced by the carbon. Carbon monoxide is not soluble in caustic soda, and is collected over water, as in the diagram.

Make the tube T red-hot by means of the furnace. Pour a little dilute hydrochloric acid down the funnel on to the marble in F. This will drive a *slow* current of carbon dioxide

over the red-hot charcoal in T. A quantity of carbon monoxide will collect in the jar J.

When sufficient gas has been collected disconnect the flask F and cease the heating. Examine the gas according to the
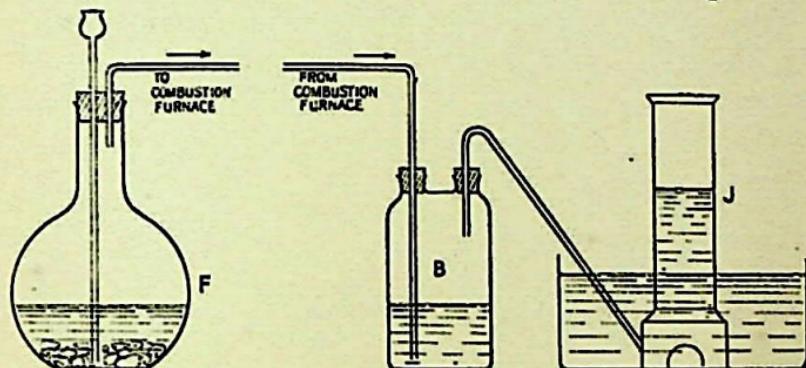
Fig. 95.—Reduction of Carbon Dioxide

F, Flask for generating carbon dioxide. B, Wash-bottle containing caustic soda. J, Gas jar for collecting carbon monoxide.

usual scheme (p. 46). Also light a jar full of the carbon monoxide, allow it to burn, and then shake up the gas remaining in the gas-jar with lime-water. Note the milkiness produced, due to the formation of calcium carbonate.

Experiment 107.—To reduce carbon dioxide by means of iron.
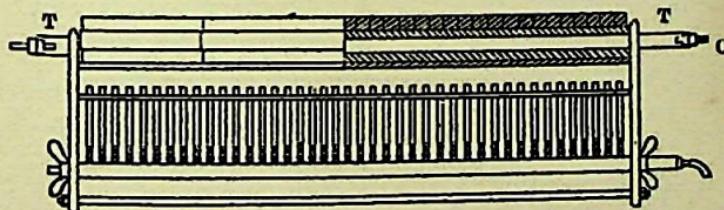
Fig. 96.—Reduction of Carbon Dioxide : Combustion Furnace

Repeat Experiment 106, using iron turnings in the tube T (fig. 96) in place of carbon.

Preparation of Carbon Monoxide.—Carbon monoxide may

be prepared by passing a slow stream of carbon dioxide over heated carbon or iron.

$$CO_2 \begin{array}{c} \text{carbon} \\ \text{dioxide} \end{array} + \text{carbon} \Big\} \text{form} \begin{cases} \text{carbon} \\ \text{monoxide.} \end{cases} CO$$

$$CO_2 \begin{array}{c} \text{carbon} \\ \text{dioxide} \end{array} + \text{iron} \Big\} \text{form} \begin{cases} \text{magnetic oxide} \\ \text{of iron} \end{cases} + \begin{array}{c} \text{carbon} \\ \text{monoxide.} \end{array} CO$$
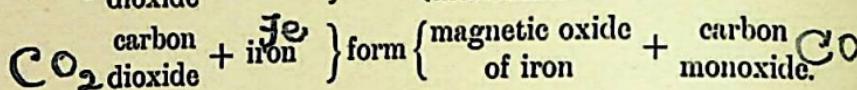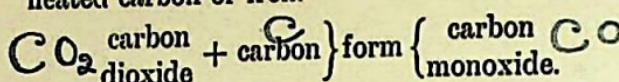
Carbon monoxide is also formed when carbon burns in a limited supply of air. In an ordinary fire the coal or coke at the bottom of the grate burns and forms carbon dioxide. This carbon dioxide is reduced to carbon monoxide as it passes through the red-hot coke in the centre of the fire. The carbon monoxide so formed burns on the top of the fire with a blue flame, again forming carbon dioxide. In the manufacture of iron from iron oxide in a blast-furnace large quantities of carbon monoxide are produced. The iron oxide is reduced in the furnace by means of coke. The coke (carbon) is at the same time oxidized to carbon monoxide (see p. 294). When steam is passed over red-hot carbon the carbon reduces the steam to hydrogen, and is itself oxidized to carbon monoxide.

$$H_2O \begin{array}{c} \text{water} \\ \text{vapour} \end{array} + \text{carbon form hydrogen} + \begin{array}{c} \text{carbon} \\ \text{monoxide.} \end{array} CO$$
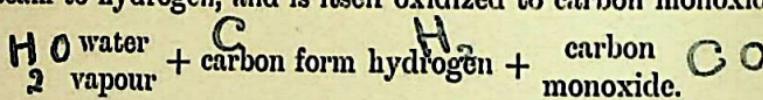
The mixture of hydrogen and carbon monoxide thus produced is called "water-gas", and is used as a fuel in some cases.

The usual laboratory methods of preparing carbon monoxide are:—

(i) By heating concentrated sulphuric acid with formic acid. The sulphuric acid acts as a dehydrating agent—that is, it withdraws the elements of water from the formic acid, and carbon monoxide is left.

formic acid decomposes into water + carbon monoxide.

(ii) *By heating concentrated sulphuric acid with oxalic acid.*
The sulphuric acid acts as a dehydrating agent. When the elements of water have been removed from oxalic acid a mixture of carbon monoxide and carbon dioxide is left. The

mixture of the two oxides of carbon is passed through a solution of caustic soda. This will absorb the carbon dioxide and allow the carbon monoxide to be collected alone.

$$\left.\begin{array}{c}\text{oxalic}\\\text{acid}\end{array}\right\}\begin{array}{c}\text{decomposes}\\\text{into}\end{array}\left\{\text{water} + \begin{array}{c}\text{carbon}\\\text{monoxide}\end{array} + \begin{array}{c}\text{carbon}\\\text{dioxide}.\end{array}\right.$$
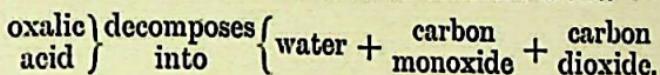
(iii) *By heating sulphuric acid with potassium ferrocyanide.*

In this case carbon monoxide and sulphates of potassium, iron, and ammonium are formed. Use a large flask, as the action is often very violent, and otherwise is apt to get out of control.

Experiment 108.—To prepare carbon monoxide from oxalic acid.

Place 20 grm. of crystallized oxalic acid in the flask F (fig. 97). Cover it with concentrated sulphuric acid.
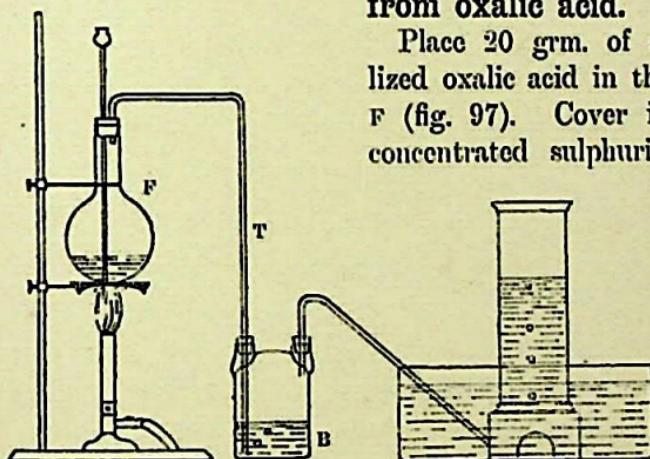
Fig. 97.—Preparation of Carbon Monoxide

Arrange the delivery-tube T so that it dips well below the surface of the caustic-soda solution in B.

Heat the contents of the flask F and collect the carbon monoxide over water.

Apply the test indicated in Experiment 106 to prove that the gas collected *is* carbon monoxide.

Properties.—Carbon monoxide is a colourless, tasteless gas. It is very poisonous, and is all the more dangerous because it has no smell. Air containing 1 per cent of carbon monoxide, if inhaled, may cause death.

Carbon monoxide is almost insoluble in water. The gas burns with a blue flame but will not support combustion.

Carbon monoxide is a strong reducing agent. If iron oxide, zinc oxide, or copper oxide is heated in a tube through which carbon monoxide is passing, the gas is oxidized to carbon dioxide, and the metallic oxide is reduced to the metal.

Composition.—I. *By volume.*—Two volumes of carbon monoxide combine with one volume of oxygen to produce two volumes of carbon dioxide.

This may be shown by collecting a measured volume of carbon monoxide in a eudiometer (fig. 98 or 42). An approximately equal volume of oxygen is then added to the carbon monoxide. The volume of the mixture is noted. The carbon monoxide is made to unite with some of the oxygen by passing an electric spark through the mixture. The eudiometer will then contain some oxygen and some carbon dioxide, but no carbon monoxide.

The carbon dioxide is removed by introducing a little caustic soda into the eudiometer. The decrease in volume which occurs when the caustic soda is placed in the eudiometer measures the volume of carbon dioxide that was produced. The volume of unused oxygen in the eudiometer is then ascertained by reading the volume of the gas remaining in the eudiometer. For example:

Fig. 98.—Eudiometer and Mercury Trough

Volume of carbon monoxide	= 20 cu. cm.
" " " " + oxygen	= 41 "
" " oxygen	= 21 "
" " gases in the eudiometer after explosion	= 31 "
" " {gas (oxygen) in eudiometer after absorption by caustic soda}	= 11 "
" " {oxygen which combined with 20 cu. cm. of carbon monoxide}	= {(21 − 11) = 10 cu. cm.

∴ 20 cu. cm. of carbon monoxide combine with 10 cu. cm. of oxygen to form 20 cu. cm. of carbon dioxide.

II. *By weight.*—The composition by weight of carbon monoxide may be found by oxidizing the carbon monoxide to carbon dioxide by means of copper oxide and collecting the carbon dioxide in caustic soda.

Dry carbon monoxide is passed over a weighed quantity of heated copper oxide. The carbon dioxide produced is passed through weighed tubes containing caustic soda.

At the close of the experiment the copper oxide and tubes of caustic soda are again weighed.

The increase in weight of the caustic soda gives the weight of carbon dioxide produced. The decrease in weight of the copper oxide gives the weight of oxygen used to form the carbon dioxide by oxidation of carbon monoxide. For example:

> Loss in weight of copper oxide = ·32 grm.
> Increase ,, ,, caustic soda = ·88 ,,
>
> ∴ ·56 grm. of carbon monoxide unites with ·32 grm. of oxygen to form ·88 grm. of carbon dioxide.

QUESTIONS ON CHAPTER XVI

1. What is meant by reduction? Illustrate your answer by reference to experiments you have performed with hydrogen, carbon, and carbon monoxide. (C. L.)

2. Describe the three different forms in which carbon occurs in nature. How would you show that carbon is a constituent of marble? (C. L.)

3. Write an account of the chemical and physical properties of carbon monoxide gas. How can this substance be prepared? (C. L.)

4. How would you prepare carbon monoxide? How would you distinguish experimentally between carbon monoxide, hydrogen, and oxygen? (C. L.)

5. Oxygen is passed separately through two red-hot tubes, one of which contains a small piece of carbon and the other a long layer of that material. Describe experiments to prove that the products formed are different, and show how you would separate one of them in a pure state from a mixture of both. (O. L.)

6. Describe in detail an experiment by which it can be proved that a diamond and a piece of graphite consist of the same substance.

7. What physical and chemical changes would ensue if an electric spark were sent through a mixture of two volumes of carbon monoxide and two volumes of oxygen?

8. What is meant by an allotropic form of an element? Describe the various allotropic forms of carbon.

CHAPTER XVII

ELEMENTARY VOLUMETRIC ANALYSIS

Quantitative interaction of acids and bases and acids and metals.

We have already seen (Chapter IX) that acids can be neutralized by bases or by metals. We will now make a quantitative study of this interaction.

The acids and bases employed are generally in the form of dilute solutions, called standard solutions—that is, solutions of which the concentration or strength is known.

(i) *A standard solution of hydrochloric acid.*

Hydrochloric acid contains equal volumes of hydrogen and chlorine (p. 133), and 1 litre of chlorine weighs $35\frac{1}{2}$ times as much as 1 litre of hydrogen.

Hence, in $36\frac{1}{2}$ grm. of hydrochloric acid there will be $35\frac{1}{2}$ grm. of chlorine and 1 grm. of hydrogen. When hydrochloric acid is acted upon by a metal or a base, the whole of the hydrogen is displaced from the acid.

Therefore $36\frac{1}{2}$ grm. of hydrochloric acid, on being neutralized by a metal or a base, will have *1 grm. of hydrogen* displaced from it.

A solution of hydrochloric acid which contains $36\frac{1}{2}$ grm. of hydrochloric acid per litre is called a normal solution.

The "active constituent" of an acid solution is the hydrogen; of a solution of a base it is the metal.

A normal solution is one which contains in 1 litre the equivalent weight in grammes of the active constituent of the compound in solution.

(ii) *A standard solution of sulphuric acid.*

With sulphuric acid it is found that 49 grm. of sulphuric acid contains 1 grm. of hydrogen, replaceable by a metal or a base.

A normal solution of sulphuric acid, therefore, contains 49 grm. of sulphuric acid per litre.

(iii) *A standard solution of sodium hydroxide.*

The equivalent weight of sodium (23 grm.) is contained in 40 grm. of caustic soda.

Hence *a normal solution of caustic soda contains 40 grm. of caustic soda per litre.*

(iv) *A standard solution of potassium hydroxide.*

The equivalent weight of potassium (39 grm.) is contained in 56 grm. of caustic potash.

Hence *a normal solution of potassium hydroxide contains 56 grm. of potassium hydroxide per litre.*

Since 1 litre of a normal solution of sodium hydroxide contains 23 grm. of sodium, and 1 litre of a normal solution of hydrochloric acid contains 1 grm. of hydrogen, therefore, when they react, the 23 grm. of sodium will just displace the 1 grm. of hydrogen from the acid (see p. 115).

Hence, *1 litre of normal sodium hydroxide will exactly neutralize 1 litre of normal hydrochloric acid*; or,

1 cu. cm. of a normal solution of sodium hydroxide will neutralize
| 1 | ,, | ,, | ,, | ,, | hydrochloric acid, or |
| 1 | ,, | ,, | ,, | ,, | sulphuric acid, |

and

1 cu. cm. of a normal solution of potassium hydroxide will neutralize
| 1 | ,, | ,, | ,, | ,, | hydrochloric acid, or |
| 1 | ,, | ,, | ,, | ,, | sulphuric acid. |

Similarly, *the equivalent weight of a metal will neutralize 1 litre of normal acid,* provided (*a*) that the acid and metal react with one another and (*b*) that the metal does not react with water; and, *of a base, the weight which contains the equivalent weight of the metal will neutralize 1 litre of normal acid.*

Thus by the use of standard solutions of acids we may determine the strength of a solution of a base or the equivalent of a metal, or the weight of a known base in a given substance, and make many other quantitative determinations. Such analysis is called *volumetric analysis.*

Preparation of Normal Solutions.

In preparing standard solutions of acids and bases the difficulty lies in the preparation of the first standard solution.

For example, concentrated hydrochloric acid and sulphuric acid both contain water, so that to weigh out the concentrated solution would not be to find the weight of the acid. Again, caustic soda and caustic potash are both very deliquescent substances (see p. 32), and so cannot be accurately weighed. Neither of these objections apply to the salt sodium carbonate, which reacts with acids as follows:—

$$\text{sodium carbonate} + \text{hydrochloric acid} \Big\} \text{form} \Big\{ \text{sodium chloride} + \text{water} + \text{carbon dioxide.}$$
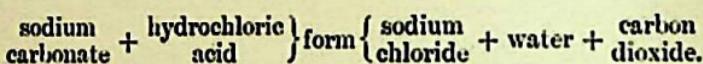
A normal solution of sodium carbonate contains 53 grm. of sodium carbonate (anhydrous) per litre, and such a solution is usually made the basis for the preparation of standard solutions of acids and alkalis.

Before proceeding to make such a solution there is one point that needs attention. It has been noticed (above) that when sodium carbonate and hydrochloric acid react, carbon dioxide is formed. We know (p. 90) that carbon dioxide dissolves in water, and that the solution reddens litmus. Thus we shall have difficulty in determining exactly when the acid has been neutralized.

We may obviate the difficulty in either of two ways.

(i) By using another indicator which is not affected by carbon dioxide, but which is affected by acids or alkalis. One such indicator is *methyl orange,* which is yellow when in alkaline or neutral solution but changes to red in the presence of free acid.

(ii) By boiling the solution of the sodium carbonate after the addition of the acid to expel the carbon dioxide from

solution. Then if the reddening of the litmus was due to the hydrochloric acid the red colour remains, but if it was due to the dissolved carbon dioxide the colour of the solution will change to blue when the carbon dioxide is expelled by boiling.

Experiment 109.—To prepare a normal solution of sodium carbonate.

NOTE.—*Distilled water is to be used in all experiments described in this chapter.*

Into a weighed watch-glass or weighing-bottle, weigh out very exactly 13·25 grm. of the purest anhydrous sodium carbonate. Wash out the salt from the watch-glass into a beaker, and dissolve it in a little warm water. Rinse the watch-glass with water, which is added to the solution in the beaker in order to prevent any loss of the sodium carbonate. Pour the solution into a 250-cu.-cm. measuring-flask (fig. 99), rinse the beaker several times with water and add the water to that in the flask. Then care-fully fill the flask with cold water to the

Fig. 99.—Measuring-flask

graduation-mark and insert the stopper. Thoroughly mix the contents of the flask by gently shaking, and if the operations have been carefully performed, and the sodium carbonate is pure, you will have a normal solution of sodium carbonate. Label the flask—
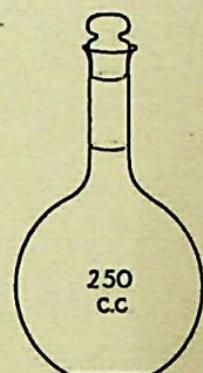
> N. sodium carbonate
> 53 grm. per litre.

and keep it for the next experiment.

Experiment 110.—To determine the strength of a solution of sulphuric acid, and to prepare a solution of normal sulphuric acid.

(i) Measure out 8 cu. cm. of concentrated sulphuric acid in a small measuring-cylinder. Add the acid *very gradually* to

about 200 cu. cm. of water contained in an ordinary flask.
Do not add the water to the acid (see p. 82). Cool the contents of the flask by holding it under a stream of cold water from the tap. When cold, transfer the solution to a 250-cu.-cm. measuring-flask, and fill the flask to the graduation-mark with cold water. You now have a dilute solution of sulphuric acid a little stronger than normal.

(ii) *To find the strength of this solution.*

Before proceeding read again p. 110.

Rinse out a burette with a few drops of the prepared solution of dilute acid, and then almost fill it with the dilute acid. Remove the air-bubbles from the tap as explained on p. 110. Transfer 10 cu. cm. of the normal sodium carbonate—prepared in Experiment 109—by means of a pipette (fig. 5), to a small beaker, and add one or two drops of methyl orange as an indicator.

See that the acid in the burette stands at 0 cu. cm. Then place the beaker on a piece of white paper, or a tile, under the burette, and allow 1 cu. cm. of the sulphuric acid from the burette to enter the beaker. Gently shake the contents of the beaker after the addition of the acid, to ensure thorough mixing of the solutions.

Continue the addition of the acid in quantities of 1 cu. cm. until the liquid in the beaker assumes a permanent red colour. Then read the level of the acid in the burette, say 9 cu. cm. You then know that the volume of acid required to neutralize 10 cu. cm. of normal sodium carbonate is more than 8 cu. cm. and less than 9 cu. cm.

(iii) *To make a more accurate determination.*

Empty the beaker and rinse it out with water. Into it place 25 cu. cm. of the normal sodium carbonate. Add to it two drops of methyl orange and place the beaker under the burette as before. Note the reading of the burette (9 cu. cm.). The results of (ii) have shown that you will require more than 20 cu. cm. of acid to neutralize 25 cu. cm. of normal sodium carbonate.

Therefore run acid into the beaker until the burette reads

29 cu. cm. Then run in the acid *one drop at a time*, with continual shaking, until a permanent red colour is obtained. Now read the level of the acid in the burette, say 29·2 cu. cm., and calculate the volume of acid required (29·2 cu. cm. — 9 cu. cm. = 20·2 cu. cm.).

Repeat (iii) twice more, and if the results of the titrations, as the above operations are called, do not differ by more than 0·1 cu. cm., the average of the three titrations may be taken as the volume of acid required to neutralize 25 cu. cm. of normal sodium carbonate.

(iv) *To calculate the strength of the acid solution.*

25 cu. cm. of normal sodium carbonate requires 25 cu. cm. of normal sulphuric acid for neutralization.

25 cu. cm. of normal sulphuric acid contains 1·225 grm. of sulphuric acid (see p. 195).

But 20·2 cu. cm. of the solution of sulphuric acid neutralized 25 cu. cm. of normal sodium carbonate.

Therefore 20·2 cu. cm. of the solution contain 1·225 grm. of sulphuric acid.

Or, 1 litre of the solution prepared contains $\frac{1·225}{20·2} \times 1000$ = 60·64 grm. of sulphuric acid per litre.

(v) *To make a normal solution of sulphuric acid.*

By means of a burette run out 80·8 cu. cm. of the acid solution which was prepared in Experiment 110 (i) into a 100-cu.-cm. measuring-flask. Fill the flask to the graduation-mark with water and the solution will be a normal one.

For 100 cu. cm. of normal sulphuric acid must contain 4·9 grm. of sulphuric acid.

But 20·2 cu. cm. of the prepared solution contains 1·225 grm. of sulphuric acid (see iv).

Therefore $\frac{4·9}{1·225} \times 20·2$ cu. cm. = 80·8 cu. cm. of the prepared acid solution will contain 4·9 grm. of sulphuric acid.

Hence, when 80·8 cu. cm. of the sulphuric acid solution is diluted to form 100 cu. cm., the solution is a normal one.

Experiment 111.—To determine the strength of a solution of caustic soda.

Make a solution of caustic soda by dissolving about 10 grm. of the solid in water and diluting it to 250 cu. cm.   Titrate the solution with the normal sulphuric acid prepared in Experiment 110 (v), using either litmus or methyl orange as an indicator, and proceeding as directed in Experiment 110 (ii) and (iii).

Calculate the strength of the solution of caustic soda as in Experiment 110 (iv).

Experiment 112.—To make a normal solution of hydrochloric acid.

Measure out 31 cu. cm. of pure concentrated hydrochloric acid and dilute it to 250 cu. cm.   Titrate it with normal sodium carbonate solution, proceeding exactly as described in Experiment 110.

Calculate the strength of the solution, and dilute it to form a normal solution of hydrochloric acid.

Experiment 113.—To find the equivalent of a metal.

Use magnesium.

Weigh out about ·3 grm., say ·305 grm., of magnesium ribbon, and dissolve it in a measured volume, say 30 cu. cm., of the normal hydrochloric acid prepared in Experiment 112.

When the metal is completely dissolved, titrate the solution of the metal in the acid with normal sodium carbonate.   By this means you will find what volume of acid was not neutralized by the metal.

Suppose the volume of normal sodium carbonate required = 4·7 cu. cm.

Then the volume of normal hydrochloric acid neutralized by the metal = 30 − 4·7 cu. cm. = 25·3 cu. cm. (see p. 195).

But 1000 cu. cm. of normal hydrochloric acid are required to neutralize the equivalent weight of the metal.

Therefore the equivalent weight of magnesium

$$= \frac{1000}{25 \cdot 3} \times \cdot 305 \text{ grm.}$$

$$= 12 \cdot 05 \text{ grm.}$$

The results of the experiments described in this chapter and of similar experiments indicate—

(i) That when an acid is neutralized by a base, combination takes place between very definite weights of the acid and of the base.

(ii) That when an acid is neutralized by a metal, a definite weight of a certain metal is required to neutralize a given weight of a particular acid.

QUESTIONS ON CHAPTER XVII

1. What is meant by a normal solution? How would you proceed to prepare a normal solution of potassium hydroxide if you were provided with a normal solution of hydrochloric acid?

2. 23·7 cu. cm. of a solution of sulphuric acid are required for complete neutralization of 25 cu. cm. of a normal solution of caustic soda. Calculate the strength of the solution of sulphuric acid.

3. In what respect can 40 grm. of caustic soda be said to be equivalent to 56 grm. of caustic potash? How would you proceed to test the truth of this statement experimentally?

4. How would you proceed to find the equivalent of zinc, given a solution of sulphuric acid of known strength? It is found that ·3 grm. of a certain metal will exactly neutralize 18·2 cu. cm. of a solution of sulphuric acid containing ·0235 grm. of sulphuric acid per cubic centimetre. Calculate the equivalent of the metal.

CHAPTER XVIII

BROMINE, IODINE, AND THEIR ACIDS

BROMINE

Bromine is a liquid which gives off a poisonous vapour. The vapour has a most irritating and disagreeable smell. For this reason it should not be allowed to escape unnecessarily into the air of the laboratory.

Experiment 114.—To prepare bromine and examine its properties.

The apparatus shown in fig. 73 may be used. Mix 20 grm. of potassium bromide with 7 grm. of manganese dioxide. Place it in the stoppered retort R. Be careful not to allow any of the mixture to get into the neck of the retort. Add 20 cu. cm. of concentrated sulphuric acid to 10 cu. cm. of water, and by means of a funnel pour the diluted acid on the mixture in the retort.

Warm the retort gently. The reddish-brown vapour that is formed will condense and collect in the receiver F, which must be kept cold by means of a stream of cold water. The reddish-brown liquid which collects in F is bromine.

Examine the vapour of bromine (the reddish-brown fumes) according to the scheme on p. 46. In testing the vapour to see whether it will support the combustion of a taper and of phosphorus, a little of the liquid bromine should be warmed in a beaker in the fume-closet and the test made in the vapour which is given off.

In addition to this examination perform the following experiments with the liquid bromine.

(i) Add a little liquid bromine to some water in a test-tube. (Does the bromine sink or float?) Shake up the bromine and water in the test-tube to obtain a solution of bromine (bromine-water).

Pour a little of the bromine-water on a piece of litmus and

a piece of coloured cloth. Leave it for some time, and then examine the paper and cloth to see whether they have been bleached by the bromine.

Make a little starch-paste by boiling $\frac{1}{2}$ grm. of starch with some water in a beaker.

Add a little of this starch-paste to some bromine-water. Notice the colour of the starch on the addition of the bromine-water. Now add a few drops of a solution of potassium iodide to the mixture of starch-paste and bromine-water. Again notice the colour of the starch.

(ii) Determine whether bromine combines directly with metals.

The metals antimony, sodium, magnesium, and copper in the form of powder or thin foil should be used. A few drops of bromine are placed in a dish, and the metals dropped on the bromine.

(iii) Determine whether hydrogen will burn in bromine vapour. To do so, proceed as with chlorine, Experiment 78, (i), p. 130.

The bromine vapour should be obtained by warming a little of the liquid in a beaker in a fume-closet.

(iv) Determine whether bromine vapour has any action upon warm turpentine. To do so, proceed as with chlorine, Experiment 78, (ii), p. 130.

The properties of bromine as just determined should now be compared with the properties of chlorine (p. 131). The points of resemblance should be carefully noted.

We have already seen that when sulphuric acid acts upon a chloride, hydrochloric acid is produced. We will next study the action of sulphuric acid upon a bromide.

Experiment 115.—To study the effect of sulphuric acid upon potassium bromide.

Place a small crystal of potassium bromide in a test-tube. Pour upon it a few drops of concentrated sulphuric acid. Warm the mixture gently. Several gases will probably be given off by the mixture. You ought to have no difficulty in identifying one of them.

Experiment 116.—To find the effect of chlorine upon a solution of a bromide.

Use potassium bromide. Dissolve a small crystal of potassium bromide in a little water in a test-tube. Add to the solution a little freshly made chlorine-water. Notice the colour of the solution due to the liberation of bromine from the potassium bromide by the chlorine.

History.—It was by a method similar to that of Experiment 116 that bromine was discovered by Balard in 1826.

Balard was examining the mother-liquor (the liquid which remains) after common salt has been removed from sea-water. In his examination he added chlorine-water to the mother-liquor, and observed the intense yellow colour of the solution which then appeared. This was due, as we now know, to the bromine set free from magnesium bromide by the action of the chlorine. [Magnesium bromide occurs in sea-water (see p. 109), but because there is so little of it in sea-water it remains in solution when the common salt has crystallized out.]

The yellow solution was then shaken up with ether, a liquid in which bromine is more soluble than it is in water. The solution of bromine in ether was then treated with caustic potash, which destroyed the yellow colour. The loss of colour was due to the action of the caustic potash upon the bromine. Caustic potash reacts with bromine to form potassium bromide and other substances.

The colourless solution, containing potassium bromide, was then distilled with sulphuric acid and manganese dioxide, and a reddish-brown liquid was obtained. This Balard called "bromine", a word which means "a stench". By careful examination of the new substance he showed that it was an element with properties similar to those of chlorine.

Properties.—Bromine is a mobile, reddish-brown liquid. It is very volatile, and gives off quantities of reddish-brown fumes at ordinary temperatures. The vapour is poisonous, and attacks the membranes of the eyes and nose, causing

severe irritation. The liquid, if it comes in contact with the skin, causes sores which do not readily heal. It is more soluble in water than chlorine, but the solution changes to hydrobromic acid much more slowly than a solution of chlorine changes to hydrochloric acid.

Bromine will not unite with hydrogen even in sunlight. In this respect it is much less energetic than chlorine, which under the same conditions combines with hydrogen violently. Bromine will however combine directly with hydrogen if a mixture of the gases is passed through a tube containing
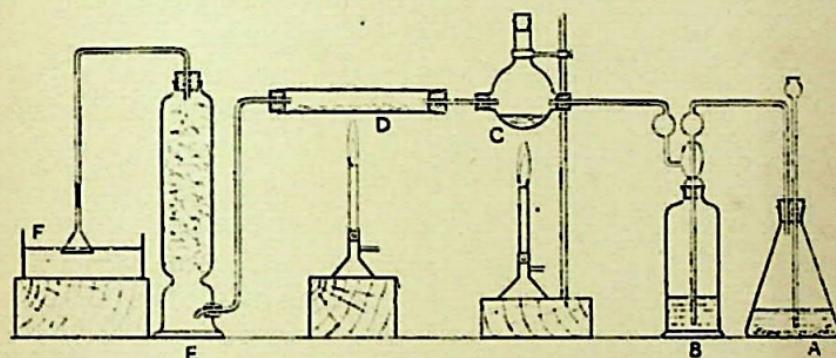
Fig. 100.—Synthesis of Hydrobromic Acid

platinized asbestos. A method of conducting the experiment is shown in fig. 100.

A contains zinc and sulphuric acid to generate hydrogen.

B contains sulphuric acid to dry the hydrogen.

C contains bromine, which is slowly vaporized by the Bunsen burner some distance below the three-necked receiver C.

D contains platinized asbestos, which is heated strongly by means of the Bunsen burner.

E contains glass-wool on which is some damp red phosphorus to absorb any bromine which has escaped combination with the hydrogen.

F contains water to absorb the hydrobromic acid which is formed by the union of the hydrogen and the bromine. The funnel serves to prevent the water in F from rushing over into E, in case the evolution of hydrogen slackens.

The air is first displaced from the apparatus by means of a stream of hydrogen. The bromine is then vaporized, and as the mixture of hydrogen and bromine passes over the hot platinized asbestos combination takes place and hydrobromic acid is formed. This dissolves in the water in F.

If dry hydrogen is passed through warm bromine the mixture of hydrogen and bromine vapour can be ignited. The gases burn and form clouds of hydrobromic acid. ·

Many metals, such as antimony, sodium, and potassium, will burn in bromine and form bromides. Metals do not, however, combine with bromine with the same vigour as they combine with chlorine to form chlorides. Bromine will support the combustion of phosphorus and of a taper. With phosphorus, bromine forms phosphorus bromides. When a taper burns in bromine vapour hydrobromic acid is formed and carbon is deposited.

Here, again, the reaction is similar to the reaction with chlorine, but it is not so energetic.

Bromine, like chlorine, possesses bleaching properties, but in a much less degree than chlorine.

Occurrence.—Bromine is never found free in nature. In combination as bromides it occurs in some mineral waters and in sea-water.

Animals and plants which live in the sea often contain bromides which they obtain from the sea-water.

The bulk of the world's supply of bromine comes from the Stassfurt deposits in Germany. These are remarkable salt-beds consisting mainly of chlorides of sodium, potassium, and magnesium, and sulphates of potassium, magnesium, and calcium.

The material in the deposits is dissolved in water and the main salts present in it are removed. The mother-liquor then contains a small percentage of bromides.

HYDROBROMIC ACID

Experiment 117.—To prepare hydrobromic acid and examine its properties.

(i) The apparatus shown in fig. 101 may be used. The funnel D is provided with a stopcock T, so that the liquid in the funnel may be introduced into the flask drop by drop. Place 5 grm. of red phosphorus, 40 grm. of fine sand, and 10 grm. of water into the flask F.

Partly fill the U-tube with glass-wool and damp red phosphorus. The glass-
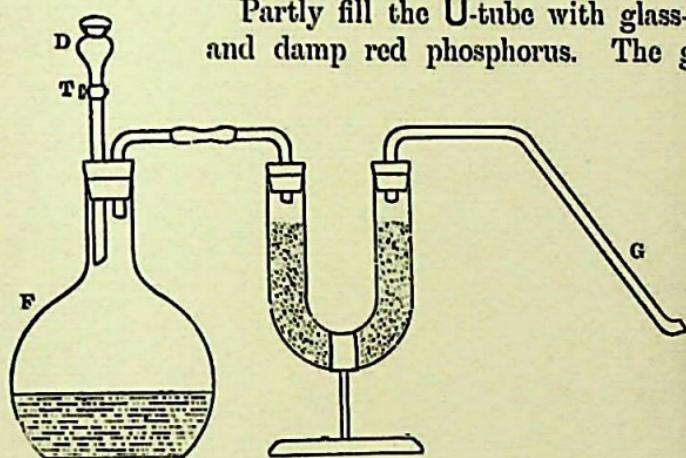
Fig. 101.—Preparation of Hydrobromic Acid

wool will prevent the phosphorus from choking up the passage through the U-tube. Red phosphorus is used in F instead of the yellow variety because the action with it is less vigorous. Even with red phosphorus it may be advisable to wrap a towel round F in case of an explosion. Place 25 grm. of bromine in the dropping-funnel D.

The delivery-tube G should be connected to a funnel which *just* dips into water (see fig. 65) if a solution of the gas is desired. Gaseous hydrobromic acid may be collected by the downward displacement of air by introducing the delivery-tube into a gas-jar containing only air. Allow the bromine to enter the flask containing the red phosphorus and water, sufficiently slowly to enable you to count the drops. Notice that the chemical combination is so energetic that a flash of

light occurs as each drop enters. Collect one or two jars full of gaseous hydrobromic acid, and then collect the remainder of the gas given off as a solution in water.

(ii) Examine the gas in the usual way (p. 46).

    (*a*) Add concentrated sulphuric acid to a little of the solution of hydrobromic acid. What happens?

    (*b*) Neutralize some of the solution of hydrobromic acid with potassium hydroxide and endeavour to obtain crystals of potassium bromide.

    (*c*) Add a few drops of silver nitrate to a solution of hydrobromic acid. Notice the colour of the silver bromide which is precipitated. Find whether the silver bromide will dissolve in ammonia.

Experiment 118.—To find the effect of sulphuretted hydrogen on bromine in the presence of water.

Place a drop of bromine in a test-tube with some water.

Pass sulphuretted hydrogen through the liquid. · Notice the precipitate of sulphur which forms. Show that it is sulphur by filtering the solution and burning the sulphur which collects on the filter-paper.

Test the filtrate for hydrobromic acid by test (*c*), Experiment 117 (ii).

Preparation.—Hydrobromic acid can be prepared directly from its elements. Two methods of so doing have already been discussed (see pp. 205 and 206).

The usual laboratory method of preparation is by the action of phosphorus upon bromine. Phosphorus combines with bromine and forms phosphorus tribromide and phosphorus pentabromide. Both these bromides are decomposed by water with the formation of phosphorous acid and hydrobromic acid.
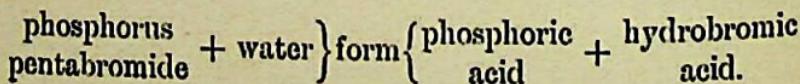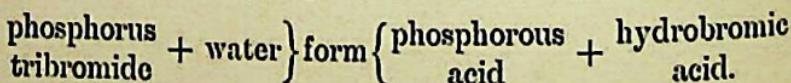
$$\left.\begin{matrix}\text{phosphorus}\\\text{tribromide}\end{matrix} + \text{water}\right\}\text{form}\left\{\begin{matrix}\text{phosphorous}\\\text{acid}\end{matrix} + \begin{matrix}\text{hydrobromic}\\\text{acid.}\end{matrix}\right.$$

$$\left.\begin{matrix}\text{phosphorus}\\\text{pentabromide}\end{matrix} + \text{water}\right\}\text{form}\left\{\begin{matrix}\text{phosphoric}\\\text{acid}\end{matrix} + \begin{matrix}\text{hydrobromic}\\\text{acid.}\end{matrix}\right.$$

Hydrobromic acid cannot be obtained by the action of concentrated sulphuric acid upon a bromide. This is due to the fact that sulphuric acid decomposes hydrobromic acid, forming bromine, while the sulphuric acid is itself reduced to sulphur dioxide. Thus the products of the action of concentrated sulphuric acid upon a bromide are hydrobromic acid, sulphur dioxide, water, and bromine.

$$\left.\begin{array}{c}\text{potassium}\\\text{bromide}\end{array} + \begin{array}{c}\text{sulphuric}\\\text{acid}\end{array}\right\} \text{form} \left\{\begin{array}{c}\text{potassium}\\\text{sulphate}\end{array} + \begin{array}{c}\text{hydrobromic}\\\text{acid.}\end{array}\right.$$

$$\left.\begin{array}{c}\text{hydrobromic}\\\text{acid}\end{array} + \begin{array}{c}\text{sulphuric}\\\text{acid}\end{array}\right\} \text{form} \left\{\text{bromine} + \begin{array}{c}\text{sulphur}\\\text{dioxide}\end{array} + \text{water.}\right.$$
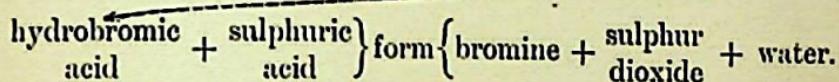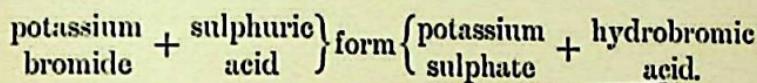
Phosphoric acid may however be used instead of sulphuric acid without decomposing the hydrobromic acid formed.

Hydrobromic acid is also formed when sulphuretted hydrogen or sulphur dioxide is passed into bromine in water.

$$\left.\begin{array}{c}\text{sulphuretted}\\\text{hydrogen}\end{array} + \text{bromine}\right\} \text{form} \left\{\begin{array}{c}\text{hydrobromic}\\\text{acid}\end{array} + \text{sulphur.}\right.$$
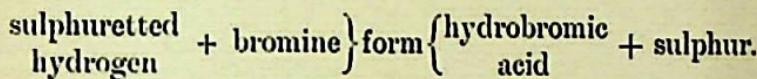
In the case of sulphur dioxide the reaction goes further, and bromine is formed again. The bromine oxidizes the solution of sulphur dioxide (sulphurous acid) into sulphuric acid, and is itself reduced to hydrobromic acid. The sulphuric acid then reacts with the hydrobromic acid as above and forms bromine.

Properties.—Hydrobromic acid is a colourless gas with a characteristic smell. It fumes in moist air and is very soluble in water. In its chemical properties the gas is much like hydrochloric acid, the properties of which should be read again. The reactions with hydrobromic acid, however, are not so energetic as the corresponding reactions with hydrochloric acid.

IODINE

Experiment 119.—To prepare iodine and examine its properties.

(i) Use the same apparatus as was used in the preparation of bromine (fig. 73).

Proceed in exactly the same manner as in the preparation of bromine, except that potassium iodide must be used in place of potassium bromide.

(ii) (a) Notice the appearance, colour, and smell of the crystals of iodine which collect in the receiver. Observe also the colour of the vapour of iodine as the iodine is distilled.

(b) Try to make a solution of iodine. If the solid is insoluble in water, try, in turn, chloroform, carbon bisulphide, and a solution of potassium iodide in water. Notice the colours of the solutions obtained.

(c) Use the solution of iodine in potassium iodide to determine whether iodine possesses bleaching properties. To do so, the effect of the solution upon litmus or coloured cloth should be observed.

The effect of the solution of iodine in potassium iodide upon starch should also be determined.

(d) Warm a few crystals of iodine in a beaker in a fume-closet. Determine whether (i) the vapour will burn, (ii) the vapour will support the combustion of a taper or of phosphorus.

(e) Warm a little iodine in a test-tube with a small piece of antimony, magnesium, or a drop of mercury. Does the iodine attack the metal?

Compare and contrast the properties of iodine with those of chlorine and bromine.

Experiment 120.—To study the effect of sulphuric acid upon potassium iodide.

Proceed exactly as in Experiment 115, but use potassium iodide in place of potassium bromide.

Compare the result with the action of sulphuric acid upon (i) a chloride, (ii) a bromide.

Experiment 121.—To find the effect of (i) chlorine, (ii) bromine, upon a solution of an iodide.

Proceed exactly as in Experiment 116, using first chlorine-water, and then, separately, bromine-water.

Properties.—Iodine is a dark bluish-black crystalline solid. It is only slightly volatile at ordinary temperatures. When heated, the solid is converted into a beautiful violet vapour.

Iodine is only slightly soluble in water. The solution in water is of a faint-brown colour. Iodine is much more soluble in a solution of potassium iodide. The solution is brown, as also are the solutions of iodine in alcohol and ether. Carbon bisulphide and chloroform will also dissolve iodine, but the solutions formed are violet in colour.

The explanation of the differences in colour of the various solutions of iodine is probably as follows. In the violet solutions the iodine exists as free iodine, whereas in the brown solutions the iodine has united with the solvent to form a new substance,

Iodine will not unite with hydrogen unless passed over heated platinized asbestos. In this respect iodine is even less energetic than bromine, for hydrogen and bromine will ignite if the mixture is brought into contact with a flame.

Iodine vapour will not support the combustion of a taper. Phosphorus, however, will burn in iodine vapour, forming iodides of phosphorus.

Like chlorine and bromine, iodine has a great affinity for metals. If antimony powder be dropped into iodine vapour the antimony burns and forms antimony iodide. Similarly, if mercury and iodine are heated together a vigorous reaction takes place, and mercuric iodide is formed.

Unlike chlorine and bromine, iodine is not a powerful oxidizing agent, and it does not therefore possess bleaching properties.

Occurrence.—Iodine is not found free in nature. It occurs in combination chiefly as iodides and iodates.

Sea-weeds contain iodine from about ·05 per cent to ·5 per cent of the weight of the dry weed. To extract it, the sea-weed is burnt and the ash mixed with water. On concentrating the solution the less soluble salts crystallize out but the iodides remain in solution. These are treated with sulphuric acid and manganese dioxide in stills, and the iodine which is liberated distils over and is collected. (See Experiment 119.)

Iodine is also found as sodium iodate, an impurity in Chili saltpetre. The iodate is only present in the sodium nitrate to the extent of 2 parts in 1000, but since the amount of Chili saltpetre used is so enormous, the iodine obtained from it forms the main source of the world's supply.

History.—Iodine was discovered in 1812 by Courtois, a French manufacturer of saltpetre. Courtois used the ashes of sea-weed, which contain large quantities of sodium and potassium salts, to change calcium nitrate into saltpetre by double decomposition. The double decomposition was carried out in copper vats. The copper corroded very badly, and Courtois traced the cause to the sea-weed ash. He therefore dissolved the ash in water and concentrated the solution. When the potassium and sodium sulphates, sodium chloride, and sodium carbonate had crystallized out, he heated the mother-liquor with sulphuric acid in the hope of getting some indication of the substance which caused the corrosion of the copper. What he did obtain was a violet vapour. He communicated his discovery to Gay-Lussac, a famous French chemist, who in 1814 published a full account of the new element, which he called "iodine", a word which means "violet".

HYDRIODIC ACID

Experiment 122.—To prepare hydriodic acid and to examine its properties.

Use the same apparatus as was used in the preparation of hydrobromic acid (fig. 101). Place the iodine and red phosphorus in the flask, and water in the dropping-funnel. Allow

the water to drop slowly upon the mixture, proceeding as in Experiment 117. Collect the hydriodic acid first by downward displacement of air, and then as a solution in water.

Apply to the hydriodic acid tests similar to those you applied to the hydrobromic acid.

Compare and contrast the properties of the two acids.

Experiment 123.—To find the effect of sulphuretted hydrogen on iodine in the presence of water.

Repeat Experiment 118, using a crystal of iodine in place of the bromine. Test for the presence of hydriodic acid by means of silver nitrate, which gives a yellow precipitate (silver iodide) which is insoluble in ammonium hydroxide.

Preparation.—Hydriodic acid can be made by the direct combination of hydrogen and iodine (see p. 211). The usual laboratory method of preparation is by the action of phosphorus on iodine. Phosphorus combines with iodine and forms phosphorus tri-iodide and phosphorus penta-iodide. Both these iodides are decomposed by water with the formation of one of the acids of phosphorus and hydriodic acid.

$$\left.\begin{matrix}\text{phosphorus} \\ \text{tri-iodide}\end{matrix} + \text{water} \right\} \text{form} \left\{\begin{matrix}\text{phosphorous} \\ \text{acid}\end{matrix} + \begin{matrix}\text{hydriodic} \\ \text{acid.}\end{matrix}\right.$$

$$\left.\begin{matrix}\text{phosphorus} \\ \text{penta-iodide}\end{matrix} + \text{water} \right\} \text{form} \left\{\begin{matrix}\text{phosphoric} \\ \text{acid}\end{matrix} + \begin{matrix}\text{hydriodic} \\ \text{acid}\end{matrix}\right.$$
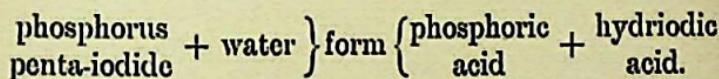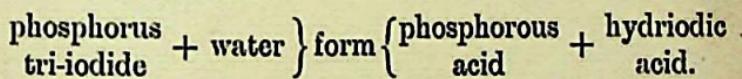
Hydriodic acid, like hydrobromic acid, cannot be obtained by the action of concentrated sulphuric acid upon an iodide. This is due to the fact that sulphuric acid decomposes hydriodic acid with the formation of iodine. The sulphuric acid itself is reduced to sulphur dioxide.

$$\left.\begin{matrix}\text{potassium} \\ \text{iodide}\end{matrix} + \begin{matrix}\text{sulphuric} \\ \text{acid}\end{matrix}\right\} \text{form} \left\{\begin{matrix}\text{potassium} \\ \text{sulphate}\end{matrix} + \begin{matrix}\text{hydriodic} \\ \text{acid.}\end{matrix}\right.$$

$$\left.\begin{matrix}\text{hydriodic} \\ \text{acid}\end{matrix} + \begin{matrix}\text{sulphuric} \\ \text{acid}\end{matrix}\right\} \text{form} \left\{\text{iodine} + \begin{matrix}\text{sulphur} \\ \text{dioxide}\end{matrix} + \text{water.}\right.$$
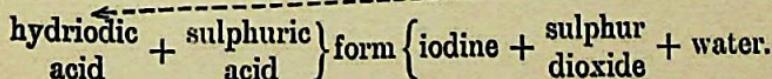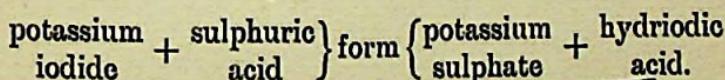
Phosphoric acid may be used in place of sulphuric acid without decomposing the hydriodic acid formed.

An aqueous solution of hydriodic acid is obtained by passing sulphuretted hydrogen through water containing iodine in suspension.

$$\left.\begin{array}{c}\text{sulphuretted}\\\text{hydrogen}\end{array}\right\} + \text{iodine}\Big\} \text{ form} \left\{\begin{array}{c}\text{hydriodic}\\\text{acid}\end{array} + \text{sulphur.}\right.$$
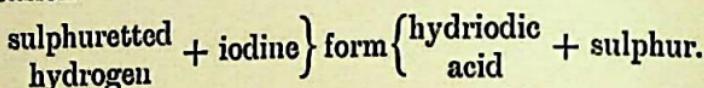
Properties.—Hydriodic acid is a colourless gas which fumes strongly in air. It is very soluble in water and the solution is strongly acid. The term "hydriodic acid" is sometimes used only for the solution of the gas. The gas itself is then known as "hydrogen iodide".

The solution is colourless when made, but turns brown owing to the decomposition of the hydriodic acid with the formation of iodine.

hydriodic acid + oxygen form water + iodine.

The action of light or of a red-hot wire is enough to decompose hydrogen iodide into its elements.

hydrogen iodide forms hydrogen + iodine.
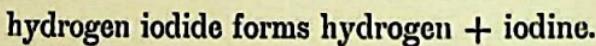
The ease with which it is decomposed, with the liberation of nascent hydrogen, makes hydriodic acid a strong reducing agent.

THE HALOGENS

Chlorine, bromine, iodine, and another element named fluorine are called halogens. The word "halogen" means "sea-salt producer". The name was given to them because (i) they all are found in sea-water, (ii) the sodium salts are very much like sea-salt (sodium chloride).

The resemblance between the properties of corresponding compounds is not confined to the sodium salts, but is noticeable in all corresponding compounds, and also in the elements themselves.

The similarity in the chemical properties of chlorine, bromine, and iodine has already been referred to.

Some of the more important properties are tabulated below, to enable a comparison to be made more readily.

	Chlorine.	Bromine.	Iodine.
Physical state	gas	liquid	solid.
Density (water = 1)	·003	3·18	4·95.
Melting-point	− 102° C.	− 7° C.	114° C.
Boiling-point	− 34° C.	59° C.	200° C.
Solubility (in grammes per 100 grm. of water) at 0° C. ...	1·47	4·3	·32
Bleaching properties	very powerful	less powerful	none.
Combination with hydrogen brought about by	light	flame	heated platinized asbestos.
Affinity for metals	very great	great	less.
Element displaced from compounds by	—	chlorine	chlorine or bromine.

It will be noticed that there is a *gradual transition* of chemical and physical properties as we pass from chlorine to iodine. For example, the ease with which the elements combine with hydrogen gets less. At the same time the melting-points of the elements get higher, and so do the boiling-points. The ease with which the elements combine with metals, however, gets less.

If we now compare the acids—hydrochloric, hydrobromic, and hydriodic acid—we find the same two characteristics:

(i) The acids have very similar properties.

(ii) They show a gradual transition of properties.

To enable a comparison of the properties of the halogen

acids to be made more readily, a few of the properties which illustrate what has been said above are tabulated below.

	Hydrochloric Acid.	Hydrobromic Acid.	Hydriodic Acid.
Boiling-point ...	− 84° C.	− 65° C.	− 34° C.
Melting-point ...	− 116° C.	− 87° C.	− 51° C.
Solubility	42 %	49 %	57 %
State	colourless gas	colourless gas	colourless gas.
Fumes in air or not...	fumes	fumes	fumes.

A comparison of the corresponding salts of these acids shows the same similarity in the properties and gradual increase in the values of the physical constants of the members. Take, for example, the potassium salts.

	Potassium Chloride.	Potassium Bromide.	Potassium Iodide.
Density	2	2·7	3·0
Solubility ...	36	65	144
Form	cubical crystals	cubical crystals	cubical crystals.

QUESTIONS ON CHAPTER XVIII

1. Give as full an explanation as you can of the reasons for classifying chlorine with bromine. How does iodine differ in its chemical properties from chlorine and bromine? (C. L.)

2. Describe the preparation of an aqueous solution of (a) hydrobromic acid, (b) hydriodic acid. How would you prepare a specimen of gaseous hydrochloric acid? (C. L.)

3. How is iodine obtained? Describe its chief chemical and physical properties. How may (a) hydriodic acid, (b) potassium iodide, be prepared from iodine? (C. L.)

4. Describe the preparation and compare the properties of

the three compounds of hydrogen with chlorine, bromine, and iodine. (O. L.)

5. What do you know of the element bromine and of its compound with hydrogen? Assuming that bromine is quite analogous to chlorine, what reactions would you expect to occur when a solution of bromine in water is added to one of caustic potash? (O. L.)

6. Starting with iodine, how would you prepare gaseous hydriodic acid? (O. L.)

CHAPTER XIX

PHOSPHORUS AND ITS COMPOUNDS

Precautions to be observed in the use of phosphorus have already been given (see foot-note on p. 39). Phosphorus is poisonous, so is its vapour.

In the following experiments a very small quantity of phosphorus should be employed, and great care should be exercised that all unburnt phosphorus is replaced in the bottle.

Experiment 124. — To compare the properties of red and yellow phosphorus.

Obtain specimens of the two varieties of phosphorus and examine them as directed below.

(i) Notice the colour and the appearance of the end of a freshly cut stick of yellow phosphorus. Compare it with the appearance of the red variety. If possible examine the appearance of both varieties in the dark.

(ii) Place a small piece of yellow phosphorus in a test-tube half-full of water. Cautiously warm the water and by means of a thermometer find at what temperature the phosphorus melts.

If the experiment is repeated with red phosphorus it will be found that the red variety remains solid even when the water is boiling.

(iii) Place small fragments of both varieties of phosphorus

upon a sand-bath. Place the Bunsen burner under the bath, and notice the time which elapses before the different kinds of phosphorus ignite. Why is it unnecessary to preserve red phosphorus under water? Notice the dense white clouds of phosphorus pentoxide which are given off as the phosphorus burns.

(iv) Take ·5 cu. cm. of carbon bisulphide in a test-tube. *Remember that this liquid is very inflammable* (see p. 23). Warm the carbon bisulphide by means of a beaker of warm water.

Dissolve a fragment of yellow phosphorus in the warm carbon bisulphide. Pour the solution upon a piece of blotting-paper. Be extremely careful not to spill any of the solution upon your clothes, or the result might be serious. Place the blotting-paper aside, and in a short time it will burst into flame.

Repeat the experiment with red phosphorus. Is the red variety soluble in carbon bisulphide?

(v) Place a little phosphorus in a bottle and cover it with either copper sulphate or silver nitrate solution. Allow it to stand for a few days. Notice the change which has occurred in the solution. Can you explain this change?

(vi) Add a fragment of phosphorus to a little *dilute* nitric acid in a flask. Notice the brown fumes given off. What does this indicate?

When the reaction has ceased, test the solution for phosphoric acid as follows.

Add strong nitric acid and ammonium molybdate solution to the liquid left in the flask and warm it. If phosphoric acid is present a yellow precipitate will form.

(vii) Boil a strong solution of caustic soda in an evaporating-dish. Add a *very* small piece of phosphorus to the solution. Notice that bubbles of gas are given off which burn when they escape from the liquid into the air. Observe the garlic-like smell of this poisonous gas. It is called *phosphine* or *phosphoretted hydrogen.*

Now write down the properties of red and yellow phosphorus just determined in two columns so that they may easily be compared.

Occurrence.—Phosphorus is never found free in nature, because it is so readily oxidized by air into phosphorus pentoxide. It occurs as salts of phosphoric acid (phosphates) in many minerals. The most abundant phosphate is calcium phosphate. Bones contain a large percentage of calcium phosphate, and bone-ash is one of the main sources of the supply of phosphorus.

Phosphates are an important manure, for phosphorus is an element which is essential to the growth of plants. Guano—the excrement of sea-birds—contains combined phosphorus and so forms an important manure.

Phosphorus is also present as sodium and ammonium phosphate in urine.

History.—Phosphorus was discovered in 1668 by Brand, an alchemist of Hamburg. Like the other alchemists, one of his aims was to find a substance which would change silver into gold. In his search he distilled urine with sand and obtained phosphorus. In 1771 Scheele obtained "Brand's phosphorus" from bone-ash.

Preparation.—Phosphorus is made from bone-ash, which contains calcium phosphate.

The bone-ash is decomposed by sulphuric acid.

$$\left.\begin{array}{c}\text{calcium}\\\text{phosphate}\end{array}\right. + \left.\begin{array}{c}\text{sulphuric}\\\text{acid}\end{array}\right\}\text{form}\left\{\begin{array}{c}\text{calcium}\\\text{sulphate}\end{array}\right. + \begin{array}{c}\text{phosphoric}\\\text{acid.}\end{array}$$
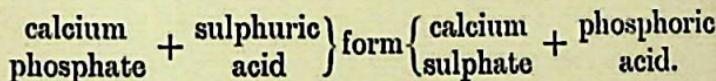
The insoluble calcium sulphate and other substances are removed by filtration and the phosphoric acid concentrated by boiling. The phosphoric acid is then reduced to phosphorus by means of charcoal as follows. The acid is mixed with charcoal and dried. It is then placed in retorts and distilled. The ends of the retorts dip into water under which the impure phosphorus collects. The gases carbon monoxide and hydrogen are formed by the reduction of the phosphoric acid, and these escape from the water.

$$\left.\begin{array}{c}\text{phosphoric}\\\text{acid}\end{array}\right. + \text{carbon}\Big\}\text{form}\left\{\begin{array}{c}\text{carbon}\\\text{monoxide}\end{array}\right. + \text{hydrogen} + \text{phosphorus.}$$
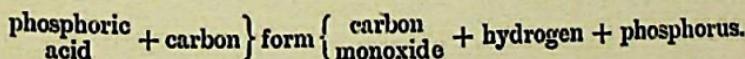
Properties.—Phosphorus exists in two allotropic modifications: (i) a yellow or white crystalline variety, and (ii) a red "amorphous" variety. The amorphous variety appears to be crystalline when viewed under the microscope.

Yellow phosphorus is a translucent almost colourless substance. If exposed to light it soon becomes coated with a white opaque crust and darkens in colour. At 0° C. it is hard and brittle. If broken, it exhibits a crystalline structure. At 15° C. it is soft and may be cut with a knife.

It melts at 44° C. and boils at 290° C. The vapour given off is very poisonous. Yellow phosphorus ignites at 30° C. and burns in air, forming dense white clouds of phosphorus pentoxide.

It is almost insoluble in water, and owing to its low ignition temperature is always kept under water. Yellow phosphorus is, however, soluble in carbon bisulphide, alcohol, and other solvents. On evaporating a solution of yellow phosphorus in carbon bisulphide, octahedral crystals of phosphorus are obtained. Similar crystals can be obtained by subliming phosphorus in a flask containing carbon dioxide or any other gas with which phosphorus does not react. If a solution of yellow phosphorus in carbon bisulphide be poured upon blotting-paper, the carbon bisulphide on evaporation leaves the phosphorus in such a finely divided state that it takes fire spontaneously.

When water containing phosphorus is boiled, the phosphorus volatilizes with the steam. If the vapour is passed through a condenser a luminous ring appears in the condenser where the phosphorus is condensed.

In air, yellow phosphorus glows with a pale-greenish light, and white fumes are given off. The phosphorescence (glowing) is due to the slow oxidation of the phosphorus. Phosphorus trioxide or phosphor*ous* oxide is formed. .

Under certain conditions, yellow phosphorus changes into an allotropic form called red phosphorus. For example, yellow phosphorus is changed to red phosphorus—

(i) By the action of air and light.

(ii) By heating it to a temperature of 250° C. in an inert gas.

(iii) By exposing it to the action of a discharge of electricity.

The reddish-brown phosphorus so obtained has several properties which differ from those of yellow phosphorus. For example—

(i) It is insoluble in carbon bisulphide and in several of the other solvents for yellow phosphorus.

(ii) It is chemically less active than the yellow variety. This is shown by the fact that it does not ignite much below 260° C. Further, it only combines with chlorine on heating, whereas yellow phosphorus ignites spontaneously when placed in chlorine.

When red phosphorus burns in air or in oxygen it forms phosphorus pentoxide. In this respect it is similar to yellow phosphorus. Also, equal weights of red and yellow phosphorus yield equal weights of phosphorus pentoxide on oxidation. Hence, red and yellow phosphorus are allotropic forms of phosphorus. Hot potassium hydroxide or sodium hydroxide is acted upon by phosphorus with the formation of phosphine (see p. 222).

Concentrated nitric acid and phosphorus react with explosive violence. With dilute nitric acid the action is less vigorous; oxides of nitrogen are given off, and the phosphorus is oxidized to phosphoric acid.

Phosphorus unites directly with many metals.—The substances formed are called phosphides. Thus, if phosphorus be added to silver nitrate solution, silver phosphide is precipitated. When phosphorus vapour is passed over red-hot lime a mixture of calcium phosphide and calcium phosphate is formed.

Matches.—Yellow phosphorus is used in the making of matches. The phosphorus is made into a paste with glue and an oxidizing agent, such as potassium chlorate or potassium nitrate. Wooden splints are dipped into melted paraffin-wax, and then into this paste. The glue protects the phosphorus from oxidation. On rubbing the match on a rough surface the friction generates sufficient heat to ignite the phosphorus.

The potassium chlorate supplies the oxygen necessary for the combustion of the phosphorus.

Owing to the poisonous nature of the yellow phosphorus, workers in match factories are liable to a disease of the bones of the face. For this reason the use of yellow phosphorus in match-making is forbidden in Britain.

"Safety" matches have therefore replaced the ordinary friction matches. The match head is made of a mixture of oxidizing agents and antimony sulphide. To ignite safety matches they are rubbed on a prepared surface coated with red phosphorus, which is not poisonous, and antimony sulphide.

Comparison of the Properties of the Allotropic Forms of Phosphorus.

Property.	Yellow Phosphorus.	Red Phosphorus.
Colour	almost colourless	reddish-brown.
Crystalline or not	crystalline	crystalline.
Odour	odour like garlic	odourless.
Phosphorescent or not ...	phosphorescent	not phosphorescent.
Oxidizes in air or not ...	oxidizes	does not oxidize.
Melting-point	44° C.	above 500° C.
Poisonous or not	poisonous	not poisonous.
Soluble in carbon bisulphide or not	soluble	insoluble
Action on chlorine... ...	forms phosphorus chlorides without being heated	forms phosphorus chlorides only on heating.

PHOSPHINE

Experiment 125.—To prepare phosphine and to examine some of its properties.

Place 5 grm. of yellow phosphorus in the flask F (fig. 102).

Cover it with a strong solution of caustic soda. Fit up the remainder of the apparatus as shown in the diagram.

Connect the tube T, by means of a piece of rubber tubing, to the gas supply. Pass coal-gas through the apparatus in order to displace the air. If coal-gas is not available a current of carbon dioxide may be used to displace the air in F. The carbon dioxide should be generated as in Experiment 54, p. 88.
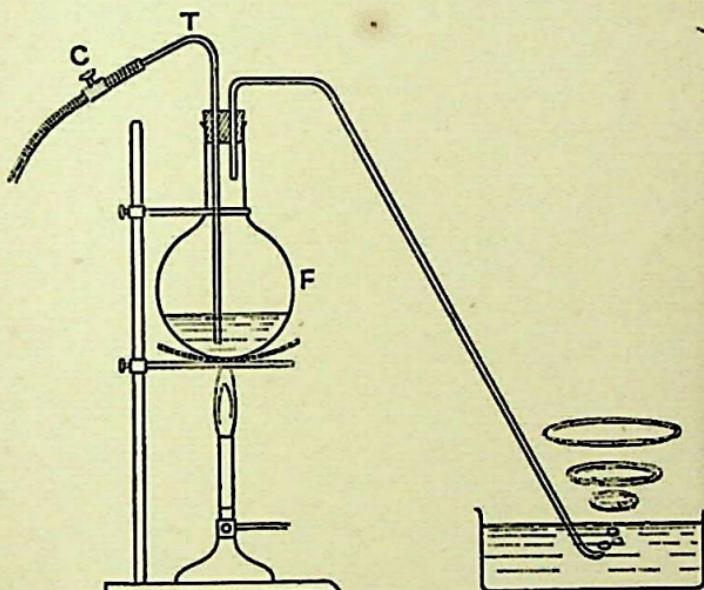
Fig. 102.—Preparation of Phosphine

When the air has been displaced from the apparatus, screw up the clip C, and proceed to heat the contents of the flask F.

Notice that the gas as it escapes into the air takes fire. It is said to be spontaneously inflammable. Notice the vortex rings of phosphorus pentoxide which leave the surface of the water as the phosphine burns. Collect a jar full of the gas over water (see Experiment 34), and then cease the heating after having removed the delivery-tube from the trough.

Notice the colour and smell of the gas. Try to make a solution of the gas in water. Test the solution with neutral litmus-paper.

Is the solution neutral or alkaline? Again displace the air

from the apparatus. Heat the solution in the flask F and pass the phosphine through (i) a solution of copper sulphate, (ii) a solution of mercuric chloride. Describe what happens in each case.

Collect a jar full of gaseous hydriodic acid, and bring it mouth to mouth with a jar of phosphine (see fig. 65). Describe what happens. Find the effect of water upon the solid produced.

Preparation.—Phosphine is prepared by the action of heated caustic soda solution upon yellow phosphorus. Milk of lime or caustic potash may be substituted for the caustic soda.

water + sodium hydroxide + phosphorus } form { phosphine + sodium hypophosphite.
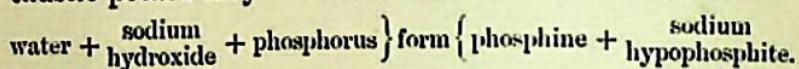
The gas so prepared is impure. Pure phosphine may be prepared by the action of caustic potash upon phosphonium iodide (see below).

potassium hydroxide + phosphonium iodide } form { phosphine + potassium iodide + water.
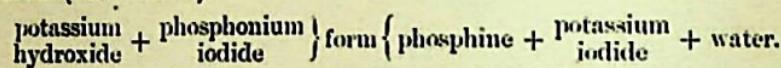
Properties.—Phosphine is a colourless, poisonous gas with a smell like that of decaying fish.

As prepared in Experiment 125 the gas is spontaneously inflammable. This is due to the presence of another compound of hydrogen and phosphorus which is formed at the same time as the phosphine. Phosphine itself is not spontaneously inflammable, but it ignites if heated to 100° C., and burns in air, forming phosphorus pentoxide.

phosphine + oxygen form { phosphorus pentoxide + water.
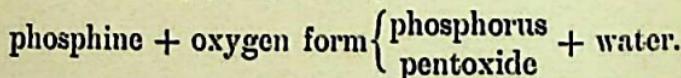
It will also burn in chlorine with the formation of phosphorus trichloride and hydrochloric acid.

Phosphine is slightly soluble in water, but the solution is not alkaline. The gas will, however, combine with gaseous hydriodic acid to form a white crystalline solid called phosphonium iodide. Similarly, by combination with hydrochloric acid or hydrobromic acid, phosphonium chloride or bromide is formed.

phosphine + hydrogen iodide form phosphonium iodide.
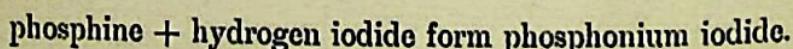
Thus, although the gas is not alkaline, it possesses basic properties (see p. 86). The phosphonium salts, however, are not very stable. At ordinary temperatures phosphonium chloride and bromide decompose into phosphine and the halogen acid. Phosphonium iodide does not dissociate to any great extent at temperatures below 30° C. Hence this is the best known of the phosphonium salts.

Phosphine is a reducing-agent. If it is passed through a solution of copper sulphate it reduces the copper sulphate to copper phosphide. The same compound is formed when phosphine is passed over heated copper. The hydrogen in the phosphine is set free. This reaction has been taken advantage of to find the composition of phosphine.

The properties of phosphine should now be compared with those of ammonia. For convenience a table of comparisons is given.

Ammonia.	Phosphine.
Stable.	Not stable. Heat decomposes it into its elements.
Very soluble in water.	Slightly soluble in water.
Solution is strongly alkaline.	Solution is not alkaline.
Unites with acids to form salts. Therefore basic.	Slight basic properties.
Burns in oxygen.	Burns in oxygen if heated to 100° C.
Unites with certain metals if heated, to form nitrides. (Water decomposes nitrides and forms ammonia.)	Unites with certain metals if heated, to form phosphides. (Water decomposes phosphides and forms phosphine.)
Ammonia is decomposed by chlorine. Nitrogen and hydrochloric acid are formed. The hydrochloric acid unites with some of the ammonia to form ammonium chloride.	Phosphine burns in chlorine. Phosphorus pentachloride and hydrochloric acid are formed. Phosphonium chloride if formed dissociates again into phosphine and hydrochloric acid.

CHLORIDES OF PHOSPHORUS

Experiment 126.—To prepare phosphorus trichloride.

Arrange the apparatus shown in fig. 103. In the flask A place manganese dioxide and hydrochloric acid from which to generate chlorine. The safety-funnel B contains hydrochloric acid in the bend of the tube. This serves to prevent
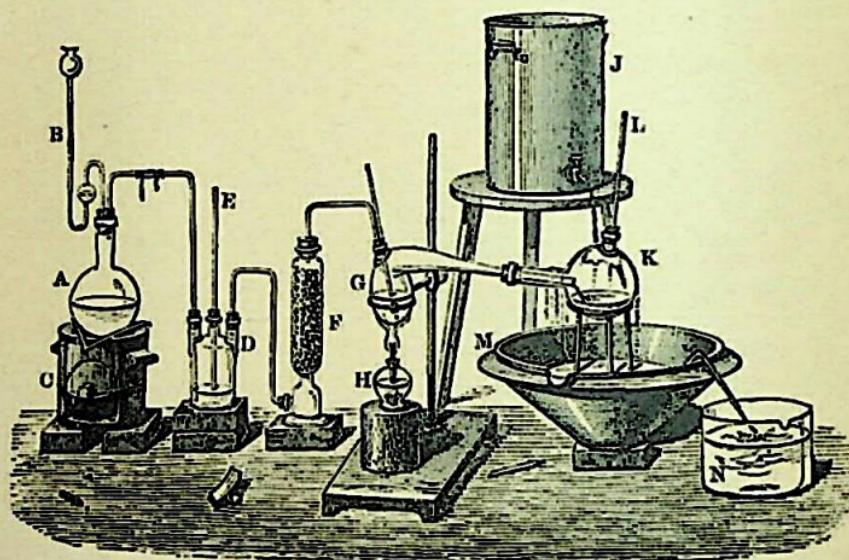
Fig. 103.—Preparation of Phosphorus Trichloride

the escape of the gas generated in A unless the pressure becomes excessive, in which case the funnel acts as a safety-valve.

The furnace C serves to heat the contents of the flask A. Of course a Bunsen burner would be equally effective.

The chlorine is dried by passing it through concentrated sulphuric acid in the wash-bottle D, and then through the tower F, containing calcium chloride. The tube E acts as a safety-valve in case the pressure in D becomes excessive. These precautions to obtain *dry* chlorine are taken because water decomposes phosphorus trichloride.

The dry chlorine is then passed over red phosphorus con-

tained in the retort G, heated by means of a spirit-lamp or Bunsen burner. In G the chlorine combines with the phosphorus, forming phosphorus trichloride, which distils over into the well-dried receiver K.

The receiver is kept cool by means of a stream of cold water from the tank J, which collects in M and siphons over into N. [The necessity for J, M, and N is done away with if the receiver is supported in the sink and the water-tap used instead of J.]

The tube L is an outlet from K for uncondensed gases or vapours and should lead to a fume-closet.

On heating the mixture in the flask A, and then gently warming the contents of the retort G, a colourless liquid—phosphorus trichloride—collects in K.

The statement—

chlorine + phosphorus form phosphorus trichloride
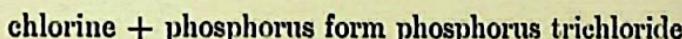
expresses the reaction which occurs when the phosphorus is in excess of the chlorine. If, however, the chlorine is in excess, another chloride of phosphorus—phosphorus pentachloride—is formed.

Properties.—Phosphorus trichloride is a mobile liquid with an unpleasant smell. The boiling-point of the liquid is 74° C., hence it gives off appreciable quantities of vapour at ordinary temperatures. The liquid fumes in air. This is due to the fact that the vapour (like the liquid) is decomposed by the moisture in the air.

water + phosphorus trichloride } form { hydrochloric acid + phosphorous acid.
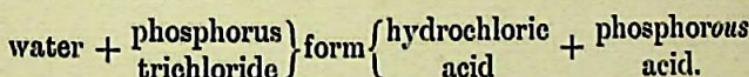
Phosphorous acid is described on p. 235.

PHOSPHORUS PENTACHLORIDE

Preparation.—By passing dry chlorine over the surface of phosphorus trichloride, combination takes place between the chlorine and the phosphorus trichloride. The liquid trichloride gradually becomes solid pentachloride of phosphorus.

During the experiment the vessel containing the phosphorus trichloride should be kept well cooled; otherwise the heat generated will vaporize the trichloride.

$$\text{chlorine} + \left.\begin{matrix}\text{phosphorus}\\\text{trichloride}\end{matrix}\right\} \text{form} \left\{\begin{matrix}\text{phosphorus}\\\text{pentachloride.}\end{matrix}\right.$$
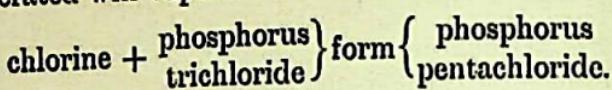
Properties.—Phosphorus pentachloride is a yellow solid. If heated it does not melt but changes directly into vapour. The vapour consists in part of a mixture of chlorine and phosphorus trichloride, and therefore is somewhat yellowish-green in colour. Thus phosphorus pentachloride vapour dissociates into chlorine and phosphorus trichloride. Dissociation is complete at 300° C. when the vapour is half chlorine and half phosphorus trichloride.

Thus not only may we write—

$$\left.\begin{matrix}\text{phosphorus}\\\text{trichloride}\end{matrix}\right. + \text{chlorine} \left.\right\} \text{form} \left\{\begin{matrix}\text{phosphorus}\\\text{pentachloride.}\end{matrix}\right.$$

but also,

$$\left.\begin{matrix}\text{phosphorus}\\\text{pentachloride}\end{matrix}\right\} \text{forms} \left\{\begin{matrix}\text{phosphorus}\\\text{trichloride}\end{matrix}\right. + \text{chlorine.}$$

Similarly,

$$\text{phosphine} + \left.\begin{matrix}\text{hydrochloric}\\\text{acid}\end{matrix}\right\} \text{form} \left\{\begin{matrix}\text{phosphonium}\\\text{chloride.}\end{matrix}\right.$$

But,

$$\left.\begin{matrix}\text{phosphonium}\\\text{chloride}\end{matrix}\right\} \text{forms} \left\{\text{phosphine} + \begin{matrix}\text{hydrochloric}\\\text{acid.}\end{matrix}\right.$$
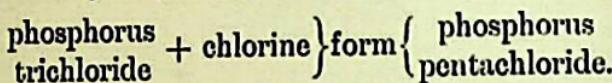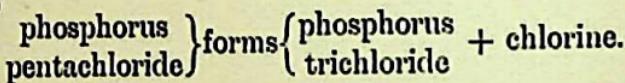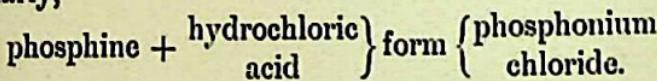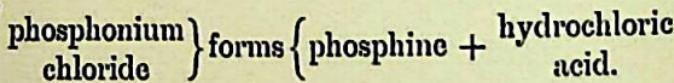
Reactions like this, which can be reversed, are spoken of as "**dissociations**", to distinguish them from reactions which cannot be reversed, and which are called "**decompositions**".

Thus we may write—

$$\text{zinc} + \left.\begin{matrix}\text{hydrochloric}\\\text{acid}\end{matrix}\right\} \text{form} \left\{\begin{matrix}\text{zinc}\\\text{chloride}\end{matrix}\right. + \text{hydrogen.}$$
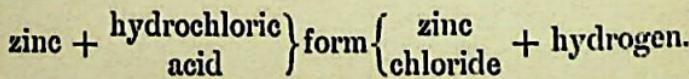
But the reverse reaction does *not* take place.

$$\left.\begin{matrix}\text{zinc}\\\text{chloride}\end{matrix}\right. + \text{hydrogen} \left\{\begin{matrix}\text{do } not\\\text{form}\end{matrix}\right\} \text{zinc} + \begin{matrix}\text{hydrochloric}\\\text{acid.}\end{matrix}$$
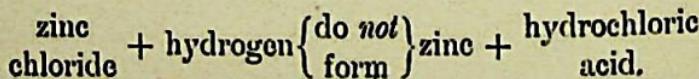
Hence, this reaction is a decomposition not a case of dissociation.

Phosphorus pentachloride fumes strongly in moist air, and is decomposed by a little water with the formation of phosphorus oxychloride and hydrochloric acid.

$$\left.\begin{array}{l}\text{phosphorus} \\ \text{pentachloride}\end{array} + \text{water}\right\} \text{form} \left\{\begin{array}{l}\text{phosphorus} \\ \text{oxychloride}\end{array} + \begin{array}{l}\text{hydrochloric} \\ \text{acid.}\end{array}\right.$$

With excess of water—

$$\left.\begin{array}{l}\text{phosphorus} \\ \text{pentachloride}\end{array} + \text{water}\right\} \text{form} \left\{\begin{array}{l}\text{phosphoric} \\ \text{acid}\end{array} + \begin{array}{l}\text{hydrochloric} \\ \text{acid.}\end{array}\right.$$
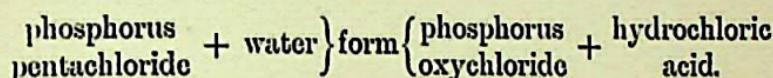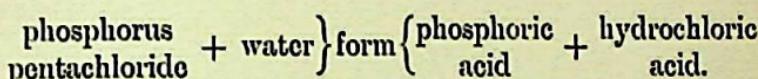
Phosphorus pentachloride is largely used in chemistry as a means of introducing chlorine into other compounds. The introduction of chlorine into water, whereby hydrochloric acid is formed, is an example. (See above.)

Similarly, chlorine can be introduced into alcohol, sulphuric acid, or acetic acid by means of phosphorus pentachloride. In each case hydrochloric acid and phosphorus oxychloride are formed during the reaction. Thus, with sulphuric acid—

$$\left.\begin{array}{l}\text{phosphorus} \\ \text{penta-} \\ \text{chloride}\end{array} + \begin{array}{l}\text{sulphuric} \\ \text{acid}\end{array}\right\} \text{form} \left\{\begin{array}{l}\text{chloro-} \\ \text{sulphuric} \\ \text{acid}\end{array} + \begin{array}{l}\text{phosphorus} \\ \text{oxy-} \\ \text{chloride}\end{array} + \begin{array}{l}\text{hydro-} \\ \text{chloric} \\ \text{acid.}\end{array}\right.$$
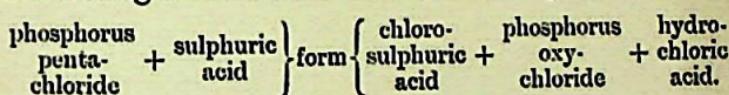
OXIDES OF PHOSPHORUS

Phosphorus Pentoxide.—We have already learnt that phosphorus burns in air or oxygen, and forms phosphorus pentoxide (see p. 50). We have further seen that this oxide dissolves in water to form phosphoric acid (p. 52). We will now study this reaction more fully.

Experiment 127.—To examine phosphorus pentoxide.

· Obtain a little phosphorus pentoxide. If necessary, this may be prepared by burning a little phosphorus contained in a deflagrating-spoon in a bell-jar.

(i) Expose a small quantity of the substance to the action

of the air by setting it aside on a watch-glass. Explain the result.

Place a piece of blue litmus-paper in the watch-glass.

(ii) Add a little phosphorus pentoxide to some *cold* water in a test-tube. Apply all the tests for acids which you know to the solution obtained (see p. 86). Test the solution for phosphoric acid as in Experiment 124 (vi). In addition to these tests neutralize the solution of phosphorus pentoxide with caustic soda. Try to name the *salt* which is then in solution.

Add a few drops of silver nitrate to the solution of phosphorus pentoxide. Notice the colour of the precipitate which forms.

If available, add a little albumen (white of egg) to a solution of phosphorus pentoxide in cold water. Shake up the mixture to see whether the albumen coagulates.

(iii) Repeat (ii) above, but either use *hot* water or boil the solution. Cool the solution before testing with albumen. Compare the results of (ii) and (iii).

(iv) Try to sublime a little phosphorus pentoxide (for instructions how to proceed refer to p. 23).

Preparation.—Phosphorus pentoxide or phosphoric anhydride (see p. 51) is formed when phosphorus burns in excess of air or oxygen.

In large quantities it may be prepared by means of the apparatus shown in fig. 104. The crucible c contains burning phosphorus. As this burns away, more phosphorus can be introduced into c by means of the tube T.

To supply the oxygen necessary for the combustion a stream of dry air is blown through the flask B by means of the bellows A. The air should be dried by means of sulphuric acid—not shown in the diagram—before entering B. The unused air escapes through E after passing through the bottle G, which serves to collect any phosphorus pentoxide not deposited in B. The phosphorus pentoxide condenses in B and falls in the form of a snow-like mass into the bottle F.

Properties.—Phosphoric anhydride is a white powder which

slowly sublimes at low temperatures.   At higher temperatures
the sublimation is much more rapid.

It is very deliquescent or hygroscopic (see p. 32).   Thus in
air it dissolves in the water which it absorbs.   When thrown
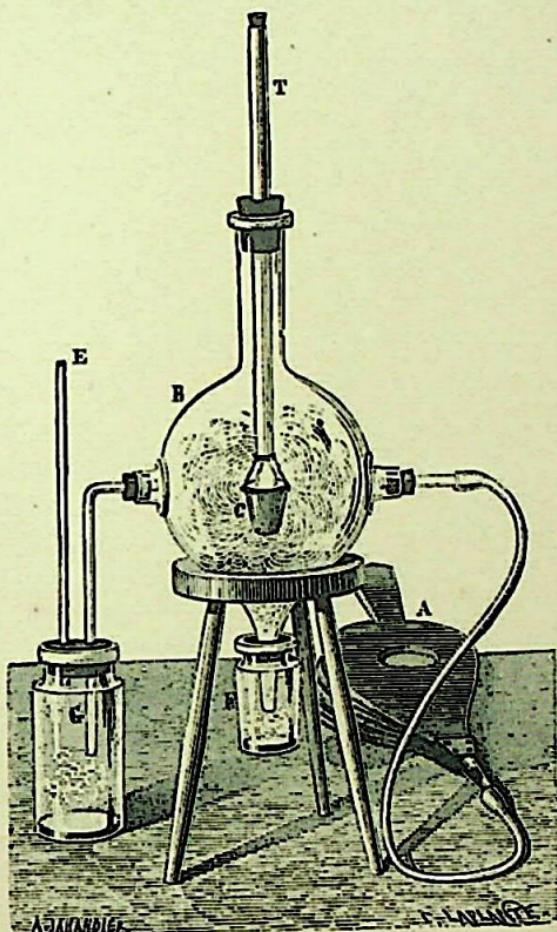
Fig. 104.—Preparation of Phosphorus Pentoxide

into water it dissolves with a hissing noise, and the water
becomes quite warm.   Because of the strong affinity for water,
phosphoric anhydride is the most effective desiccating (drying)
agent available.

When dissolved in *cold* water, phosphoric anhydride forms

*meta*phosphoric acid (see below). On boiling a solution of metaphosphoric acid another phosphoric acid called *orthophosphoric acid* is formed. These acids are described later.

If phosphoric anhydride, prepared as described above, is boiled with a solution of mercur*ic* chloride, the mercuric chloride is reduced to mercurous chloride. Mercur*ous* chloride is insoluble in water, and therefore it is precipitated as a white powder.

If, however, the phosphoric anhydride is purified by subliming it in a current of oxygen, the pure phosphoric anhydride *will not reduce mercuric chloride.*

The reducing action is therefore due to an impurity in the phosphoric anhydride. This impurity has been isolated, and is known as phosphorus trioxide or phosphor*ous* anhydride.

PHOSPHORIC ACID

We have already learnt that this acid is formed—

(i) When phosphoric anhydride is dissolved in water (above);

(ii) When phosphorus pentachloride is dissolved in water (p. 229); and

(iii) When phosphorus is oxidized by means of nitric acid (p. 221).

Now, although the neutralized solution of phosphoric anhydride in *cold* water responds to the nitric acid and ammonium molybdate test for phosphates (p. 218) similarly to the solution in *boiling* water, the two solutions behave very differently towards silver nitrate and other reagents. The *cold*-water solution forms a *white* precipitate with silver nitrate, whereas the *hot*-water solution forms a *yellow* precipitate.

Similarly, the cold-water solution of phosphoric anhydride will coagulate albumen, but the hot-water solution will not.

We are evidently here dealing with two phosphoric acids.

The solution of phosphoric anhydride in cold water is called *metaphosphoric acid*. The solution in hot water is called phosphoric acid or *orthophosphoric acid*.

There is still another phosphoric acid, called *pyrophosphoric*

acid. This is obtained when a solution of phosphoric acid is carefully heated to a temperature of 250° C. A solution of the acid so obtained answers to the ammonium molybdate test for phosphoric acid, and gives a white precipitate with silver nitrate. In these respects it is like metaphosphoric acid. It will not, however, coagulate albumen.

The differences between the three phosphoric acids have been shown to be due to the difference in the quantity of water combined with the phosphoric anhydride.

If pyrophosphoric acid be heated strongly it changes into metaphosphoric acid.

phosphoric acid — water forms pyrophosphoric acid.

pyrophosphoric acid — water forms metaphosphoric acid.

The stable form of the acid is orthophosphoric acid. Metaphosphoric acid changes gradually, but a solution of pyrophosphoric acid changes very slowly into orthophosphoric acid. Metaphosphoric acid is sold as "glacial phosphoric acid". At low temperatures it is a glass-like solid, but melts to a colourless liquid at higher temperatures.

Properties.—Phosphoric acid as obtained by any of the methods described on p. 232 is a liquid. It is easily concentrated until it becomes a viscous fluid which can with difficulty be crystallized.

The crystallized acid melts at 42° C., and is very soluble in water. The solution is acid to litmus, and forms three series of salts. The acid is therefore tri-basic (see p. 92). Thus by adding different quantities of caustic soda to phosphoric acid we can prepare—

      (i) mono-sodium phosphate.

      (ii) di-sodium phosphate.

      (iii) tri-sodium phosphate.

The last-named is the normal salt, the others are acid salts (see p. 92). The mono-sodium phosphate is acid to litmus, the di-sodium phosphate is neutral to litmus, and the tri-sodium phosphate is alkaline to litmus.

PHOSPHORUS TRIOXIDE

In the preparation of phosphorus pentoxide, described on p. 230, small quantities of a lower oxide, that is, one containing a smaller percentage of oxygen, are formed at the same time. This oxide has a much lower melting-point than the higher oxide, and advantage is taken of this fact to effect a separation of the two oxides.

Experiment 128.—To prepare phosphorus trioxide.
NOTE.—*The vapour of this substance is very poisonous.*
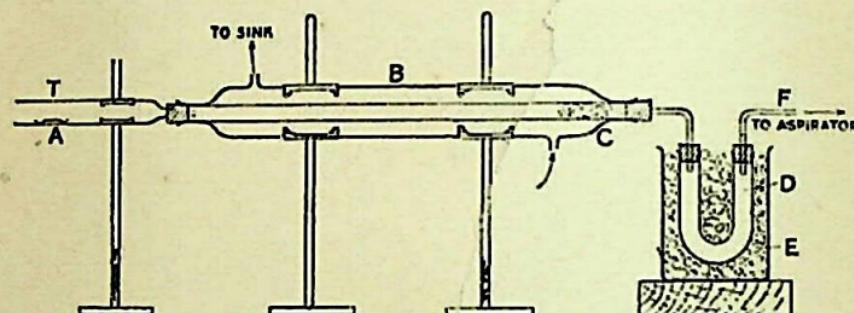
Fig. 105.—Preparation of Phosphorus Trioxide

Arrange the apparatus shown in fig. 105. The combustion-tube T contains a porcelain-boat, in which is placed a piece of yellow phosphorus, A.

The Liebig's condenser B is kept at 60° C. by means of a stream of warm water which circulates through the outer jacket. The inner tube of B contains a loose plug of glass-wool at C to arrest the phosphorus pentoxide formed by the combustion of the phosphorus.

The U-tube D, immersed in a freezing-mixture E, serves to collect the phosphorus trioxide which passes over. The tube F is connected to an aspirator, by means of which a current of dry air is drawn over the burning phosphorus. The phosphorus is ignited, and a slow stream of air is drawn through the apparatus by means of the aspirator. The phosphorus trioxide collects in the receiver as a snow-like crystalline solid.

Properties.—Phosphorus trioxide crystallizes in the form of

prisms. The crystals melt at 22° and boil at 173° C. They give off a poisonous vapour which has a garlic-like smell.

Phosphorus trioxide is readily oxidized to the higher oxide. For example, on exposure to the air oxidation gradually takes place. In chlorine or warm oxygen the oxidation is so rapid that the trioxide takes fire and burns. (The substance is said to be spontaneously inflammable).

Phosphorus trioxide dissolves in cold water to form phosphorous acid.

phosphorus trioxide + water form phosphorous acid.
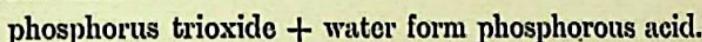
With hot water the trioxide decomposes, forming, amongst other products, phosphine and red phosphorus.

PHOSPHOROUS ACID

Phosphorous acid is formed by the action of cold water on phosphorus trioxide (see above). It is also one of the products of the action of water upon phosphorus trichloride (see p. 227).

Phosphorous acid is a crystalline solid which melts at 70° C. It is usually classed as a di-basic acid, although there seems to be some doubt on this point. The salts of phosphorous acid are called phosphites.

When heated, phosphorous acid decomposes into phosphine and phosphoric acid. This is an illustration of the reducing action of phosphorous acid. One quantity of phosphorous acid is reduced (to phosphine) in oxidizing another quantity of phosphorous acid (to phosphoric acid). Phosphorous acid will also reduce copper sulphate to copper and silver nitrate to silver, being itself oxidized to phosphoric acid.

QUESTIONS ON CHAPTER XIX

1. How are the chlorides of phosphorus prepared? What is the action of the pentachloride of water on (a) water, (b) sulphuric acid? (C. L.)

2. Describe the preparation of as pure a specimen as possible of phosphoretted hydrogen, starting with phosphorus. Compare and contrast this compound with ammonia. (C. L.)

3. How is phosphorus pentoxide obtained? What are its chemical properties? (C. L.)

4. Describe the production of phosphorus from bone-ash. How would you proceed to convert the phosphorus so obtained into its allotrope?

5. How can phosphorus be converted into phosphoric acid, and how can phosphorus be obtained from phosphoric acid?

6. Describe briefly the preparation of the different varieties of phosphoric acid. By what chemical tests could you distinguish between them?

7. What do you understand by the term "tri-basic acid"? What experimental evidence have we that phosphoric acid is tri-basic?

8. What substances are formed when phosphorus is heated (a) in air, (b) in caustic soda, (c) in dilute nitric acid?

CHAPTER XX

CRYSTALLIZATION, DIFFUSION, SOLUTION

Some of the differences between crystalline and amorphous bodies have already been noticed (see Chapter III). We will now consider the matter a little further.

It was mentioned (p. 28) that crystals are distinguishable from amorphous bodies by their geometrical shape and flat faces.

In addition to these characteristics, if several crystals of a substance are carefully examined it is found that—

(i) The angles between similar faces of the crystals are *equal*. This causes the *form* of the crystals to be the same, although corresponding faces may differ in size and shape.

(ii) The properties of the crystals are not the same in all directions. For example, light, heat, and electricity can pass through the crystal with greater ease in one direction than in another.

Experiment 129.—To separate two substances from a mixture of their solutions in water.

Make a mixture of solid copper sulphate and alum, and grind it to a powder with a pestle and mortar (fig. 106). Place about 30 cu. cm. of water in a beaker, and heat it to about 50° C. Add the powdered mixture to the warm water, a little at a time, until no more will dissolve. Stir the solution well, and after five minutes pour it into a crystallizing-dish. Allow the solution to cool. Notice that the crystals deposited are of two kinds:

(i) Crystals similar in shape to "*a*", fig. 19. These are alum.

(ii) Blue crystals of quite a different shape. These are copper sulphate.

Pick out the alum crystals and rinse them in water to free them from the mother-liquor—that is, the liquid in which they were formed. Re-dissolve the crystals in a little warm water and

Fig. 106.—Pestle and Mortar

recrystallize them. In this way pure alum crystals may be obtained. Treat the blue crystals of copper sulphate similarly, and so obtain pure copper sulphate.

Fractional Crystallization.

Imagine two substances in solution in water. As the water evaporates, the solution first becomes saturated with the less soluble substance. This substance then commences to crystallize out alone.

As evaporation proceeds the solution next becomes saturated with the more soluble substance, and then this second substance begins to crystallize out of the solution side by side with the less soluble substance.

If the substances differ greatly in solubility this is a suitable method to effect a separation of the substances. Suppose the substances in solution are (*a*) potassium chloride (very soluble) and (*b*) potassium chlorate (less soluble). The solution is concentrated until, on cooling, some of the potassium chlorate separates out. The liquid is poured off, and the first crop of

crystals (A) is collected. The evaporation is continued in another dish, and a second crop of crystals (B) is obtained. The mother-liquor (C) is retained.

A is mainly potassium chlorate. C is mainly potassium chloride in solution. B is a mixture of potassium chloride and chlorate.

If A is now dissolved in a little water and re-crystallized, the new crystals will be much purer potassium chlorate, for the little potassium chloride that was with A will remain in solution. If C is evaporated to dryness, and the solid re-dissolved in a little water, the solution obtained will contain much purer potassium chloride than the mother-liquor contains, for little of the less soluble potassium chlorate mixed with C will go into solution. By repeating these processes, very pure potassium chloride and potassium chlorate may be obtained. The whole succession of processes is called fractional crystallization.

In the manufacture of potassium chlorate the method of fractional crystallization is adopted in order to separate the potassium chlorate from the very soluble calcium chloride with which it is mixed.

Similarly, in the manufacture of potassium nitrate the common salt with which the potassium nitrate is mixed crystallizes out of the solution before the more soluble potassium nitrate, and is removed.

Diffusion.

When two liquids which can mix are placed in contact with one another a gradual mixing of the liquids takes place. This process is called *diffusion*. If a tall jar be partly filled with, say, copper sulphate solution, and water be poured gently on top of the solution of copper sulphate, the difference in colour will indicate where the solution of copper sulphate ends and the water begins.

The particles of copper sulphate begin to move very slowly into the water, and the particles of water move very slowly into the copper sulphate. The result is that in some weeks the solution in the jar has the same composition throughout.

The rate of diffusion is in this case extremely slow, but is very much increased by stirring.

The rate of diffusion varies very much with different solutions. For example: Thomas Graham (1861) found that hydrochloric acid diffuses into water about twice as quickly as common salt, six times as quickly as sugar, forty-nine times as quickly as albumen, and ninety-eight times as quickly as caramel. Substances which diffuse comparatively quickly are called *crystalloids*. Acids, most salts, and substances which crystallize are examples of crystalloids.
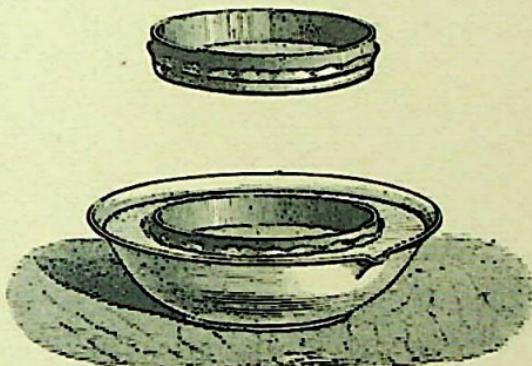
Fig. 107.—Dialyser

Substances like gum, starch, albumen, and glue diffuse very slowly, and are called *colloids*. When a crystalloid substance is dissolved in water many properties of the water are affected. For example, the boiling-point, the freezing-point, and the electrical conductivity of the water are changed. Colloid substances do not affect the solvent in this way. They do not seem to form true solutions. The colloid exists rather as a mesh or skeleton enclosing the water.

Graham also proposed and used a method by which this difference in the diffusibility of crystalloids and colloids could be utilized to separate a mixture of such substances in solution.

The solution containing the crystalloid and colloid substances is placed in a shallow dish, the bottom of which is

formed of parchment or skin (fig. 107). When the "dish" is floated upon water in a trough, the crystalloid diffuses into the water in the trough but the colloid remains in the "dish". It is essential that the distilled water in the trough be renewed every few hours.

The apparatus employed is called a dialyser, and the process is spoken of as dialysis.

Experiment 130.—To separate albumen from common salt solution by dialysis.

Add the white of an egg (albumen) to a solution of salt in water. Place the mixture in the parchment vessel, and float it on a trough of distilled water. Cover the mixture with a clock-glass. At the close of the lesson test the distilled water for common salt by means of silver nitrate. Renew the distilled water as often as possible, and in a few days the bulk of the common salt will have diffused from the parchment vessel, which will then contain only water and albumen.

Suspension and Solution.

The student is advised to refer again to p. 10, where an attempt has been made to give an elementary working definition of the term "solution". He is now reminded that no hard-and-fast line can be drawn between "suspension" and "solution".

Suspended substances will pass through the pores of some filter-papers, and it is conceivable that, with a filter with sufficiently small pores, even in colloidal "solutions" the solute could be separated from the solvent.

Again, whether a mixture of a substance with water appears clear and homogeneous or not depends upon whether the mixture is viewed by the naked eye or by means of the microscope.

A mixture which appears to be perfectly homogeneous to the naked eye may not so appear under high magnification.

To the tests for distinguishing between solution and suspension we may now add the test of diffusion.

Between the substances in *solution*, which diffuse rapidly,

and those in *suspension*, which do not diffuse at all, are the
colloids, which form colloidal "solutions" or "suspensions",
which diffuse very slowly.

CHAPTER XXI

SILICON, SILICA, AND SILICIC ACID

Silica is one of the commonest substances found in nature.
It occurs free, in the form of crystals, as quartz (fig. 108).
Sand, rock crystal,
smoky quartz, ame-
thyst, and several other
minerals are mainly
composed of silica. The
differences in colour
of these minerals are
due to the presence of
impurities.   For ex-
ample, amethyst owes
its colour to the pre-
sence of oxide of man-
ganese. Silica also oc-
curs in the amorphous
form as flint and opal.

**Experiment 131.
—To prepare amor-
phous silica.**

Fig. 108.—Quartz Crystals

Obtain some sodium or potassium silicate.   Dissolve it in
a little water and to the solution add dilute hydrochloric
acid.   Notice the gelatinous precipitate of silicic acid which is
formed.   Filter the solution and place the gelatinous precipi-
tate in a crucible and heat it over the Bunsen burner until all
the water has been expelled.   The white amorphous powder
left is silica.

(O 729) 17
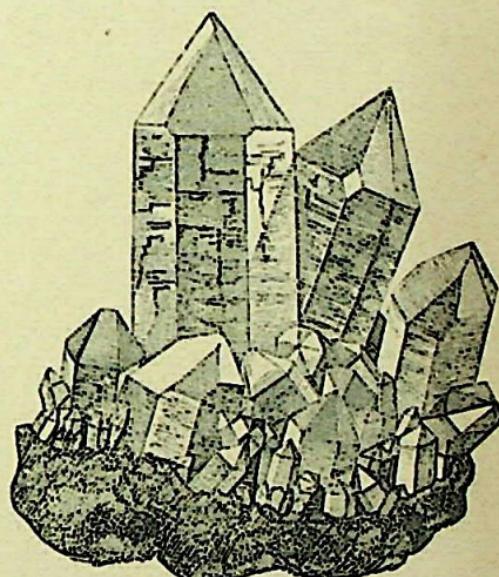
Experiment 132.—To examine the properties of amorphous silica.

Perform experiments with the amorphous silica prepared in Experiment 131 to determine whether amorphous silica is soluble in water, in acids, or in caustic soda solution. Also see whether you are able to melt amorphous silica.

Experiment 133.—To study the properties of crystalline silica.

(i) Determine whether hot concentrated acid or hot caustic soda has any effect upon crystalline silica by heating a little sand in a test-tube with hydrochloric acid, sulphuric acid, nitric acid, and caustic soda in turn.

Fig. 109.—Platinum "Boat" for Fusions

(ii) See whether you can melt crystalline silica by heating a little sand to as high a temperature as is available.

(iii) Mix a quantity of anhydrous sodium carbonate with the sand and heat the mixture as strongly as possible. The substances may be heated on a piece of platinum-foil bent into the form of a boat (fig. 109). The "boat" can then be held in the Bunsen flame by means of crucible tongs.

Notice the bubbles which rise as the silica displaces the carbon dioxide from the carbonate. Allow the mass to cool and then dissolve it in a little water. You will then have a solution of sodium carbonate and sodium silicate. To the solution add a little hydrochloric acid, and, provided the solution of sodium silicate is not too weak, a gelatinous precipitate of silicic acid will be formed.

(iv) Experiment (iii) may be repeated, using lime in place of sodium carbonate. Calcium silicate will be formed.

Experiment 134.—To prepare a solution of silicic acid.

Make a *dilute* solution of sodium silicate. Acidulate it with

hydrochloric acid.   If the solution is dilute enough the silicic
acid remains in solution; otherwise some of it is precipitated
as a gelatinous mass.   Filter the mixture if necessary in order
to obtain a clear solution.   Place the solution in a dialyser
(fig. 107) and float the dialyser upon water.   Renew the
distilled water as often as possible.   After some days the
common salt formed by the action of the hydrochloric acid
upon the sodium silicate (see below) will pass through the
membrane and a weak solution of silicic acid will remain in
the dialyser.

If left to stand for some time the solution of silicic acid
assumes the gelatinous form.

$$\left.\begin{matrix} \text{sodium} \\ \text{silicate} \end{matrix} + \begin{matrix} \text{hydrochloric} \\ \text{acid} \end{matrix}\right\}\text{form}\left\{\begin{matrix} \text{silicic} \\ \text{acid} \end{matrix} + \begin{matrix} \text{sodium} \\ \text{chloride.} \end{matrix}\right.$$
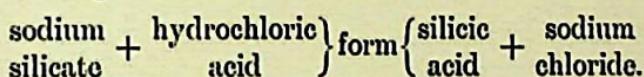
Experiment 135.—To study the formation of certain metallic silicates.

The formation of metallic silicates can be shown in an
interesting manner as follows.

Make a solution of sodium silicate in a large beaker.   Into
the beaker drop a crystal of each of various soluble salts, such
as copper sulphate, iron sulphate, nickel sulphate, and cobalt
nitrate.   Leave the beaker and its contents in a quiet place
until the next day.   It will be found that plant-like forms
of the metallic silicates will have grown in the sodium silicate.

The explanation is that the copper sulphate crystal, for
example, has dissolved in the water.   The solution of copper
sulphate and sodium silicate have then suffered double decom-
position, with the formation of copper silicate and sodium
sulphate.

$$\left.\begin{matrix} \text{copper} \\ \text{sulphate} \end{matrix} + \begin{matrix} \text{sodium} \\ \text{silicate} \end{matrix}\right\}\text{form}\left\{\begin{matrix} \text{copper} \\ \text{silicate} \\ \text{(insoluble)} \end{matrix} + \begin{matrix} \text{sodium} \\ \text{sulphate.} \\ \text{(soluble)} \end{matrix}\right.$$

Similarly,

$$\left.\begin{matrix} \text{cobalt} \\ \text{nitrate} \end{matrix} + \begin{matrix} \text{sodium} \\ \text{silicate} \end{matrix}\right\}\text{form}\left\{\begin{matrix} \text{cobalt} \\ \text{silicate} \end{matrix} + \begin{matrix} \text{sodium} \\ \text{nitrate.} \end{matrix}\right.$$
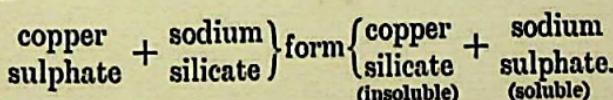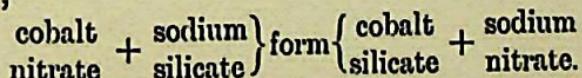
and so on.

Properties of Silica (silicon dioxide).—Silica is one of the hardest substances known. The density of the solid varies from 2.2 to 2.67. Its melting-point is also very high. Quartz, for example, does not begin to melt below 1600° C. The substance occurs in two forms. The amorphous variety is soluble in caustic soda, but crystalline silica is scarcely attacked by that reagent.

$$\left.\begin{array}{c}\text{sodium}\\\text{hydroxide}\\\text{(base)}\end{array}\right\} + \left.\begin{array}{c}\text{silicon}\\\text{dioxide}\\\text{(acid oxide)}\end{array}\right\}\text{form}\left\{\begin{array}{c}\text{sodium}\\\text{silicate}\\\text{(salt)}\end{array}\right. + \text{water.}$$
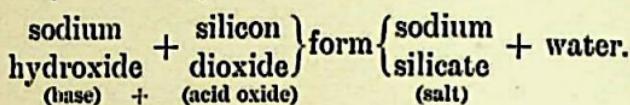
Although silica does not dissolve in water like other anhydrides, the above reaction indicates that silica is an anhydride. It is the anhydride of silicic acid and is called silicon dioxide.

The acid nature of the oxide is also shown by the fact that even crystalline silica will decompose fused sodium carbonate, with the formation of sodium silicate. Similarly, lead oxide (a basic oxide) when fused with silica forms lead silicate, a substance used in glazing pottery.

A basic oxide + *acid oxide form a salt.*
lead oxide   + silica   „ lead silicate.
calcium oxide + silica   „ calcium silicate.
sodium oxide + silica   „ sodium silicate.
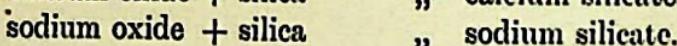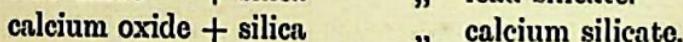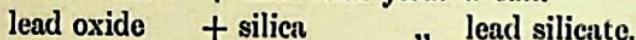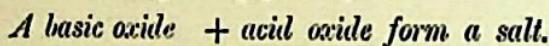
Silica is insoluble in all acids with the exception of hydrofluoric acid, an acid somewhat similar to hydrochloric acid but much more energetic.

Silica can be reduced by heating it with magnesium powder (see p. 247). Silicon, a non-metallic element, and magnesium oxide are formed.

$$\left.\begin{array}{c}\text{silicon}\\\text{dioxide}\end{array}\right\} + \text{magnesium}\left\}\text{form}\left\{\text{silicon} + \begin{array}{c}\text{magnesium}\\\text{oxide.}\end{array}\right.$$
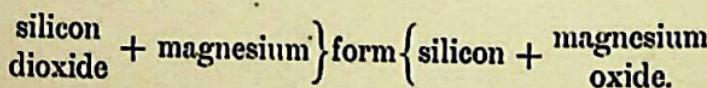
This reduction makes the connection between silicon and the silicates more apparent.

silicon (non-metal) + oxygen form silicon dioxide.
silicon dioxide + water form silicic acid.
silicic acid + base   form silicate + water.
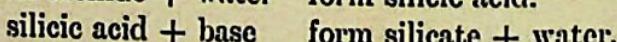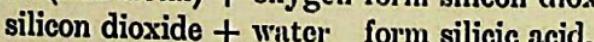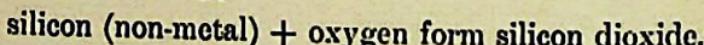
Silica acts as a weak acid oxide at low temperatures and a strong one at high temperatures. Thus at ordinary temperatures silicates dissolve in acids with the formation of silicic acid and a salt of the acid employed. For example—

$$\left.\begin{array}{c}\text{nickel}\\\text{silicate}\end{array}\right\} + \left.\begin{array}{c}\text{hydrochloric}\\\text{acid}\end{array}\right\}\text{form}\left\{\begin{array}{c}\text{nickel}\\\text{chloride}\end{array}\right. + \left.\begin{array}{c}\text{silicic}\\\text{acid.}\end{array}\right.$$
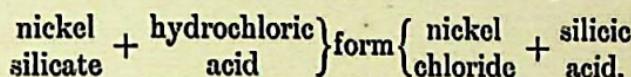
Similarly, the carbon dioxide of the air decomposes the sodium silicate contained in certain hot springs (in New Zealand) forming sodium carbonate and silicic acid.

$$\left.\begin{array}{c}\text{sodium}\\\text{silicate}\end{array}\right\} + \left.\begin{array}{c}\text{carbon}\\\text{dioxide}\end{array}\right\}\text{form}\left\{\begin{array}{c}\text{sodium}\\\text{carbonate}\end{array}\right. + \text{silica.}$$
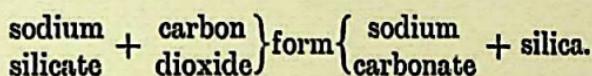
At high temperatures, however, silica displaces the acid from carbonates forming silicates. Thus silica when fused with sodium carbonate forms sodium silicate.

$$\left.\begin{array}{c}\text{sodium}\\\text{carbonate}\end{array}\right\} + \text{silica}\Big\}\text{form}\left\{\begin{array}{c}\text{sodium}\\\text{silicate}\end{array}\right. + \left.\begin{array}{c}\text{carbon}\\\text{dioxide.}\end{array}\right.$$
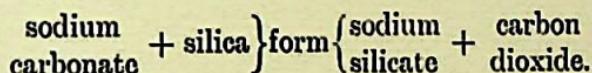
The explanation of this difference in the behaviour of silica at different temperatures lies in the fact that the other acid anhydrides are volatile (change to vapour) at high temperatures, but *silica is not volatile*. Thus when silica and carbon dioxide *compete* for the base, sodium oxide, at ordinary temperatures the carbon dioxide obtains it. But at high temperatures the carbon dioxide is driven off as a vapour, and the silica has no other competitor for the base. Hence the silicate is then formed.

SILICIC ACID

There are several silicic acids composed of silica united with water in different proportions. They are comparable with, but more complex than, the different phosphoric acids studied (see p. 232).

Orthosilicic acid has never been prepared in a pure state.

A dilute solution of the acid may be prepared by adding hydrochloric acid to a weak solution of sodium silicate.

$$\begin{matrix} \text{sodium} \\ \text{silicate} \end{matrix} + \begin{matrix} \text{hydrochloric} \\ \text{acid} \end{matrix} \Big\} \text{ form } \Big\{ \begin{matrix} \text{sodium} \\ \text{chloride} \end{matrix} + \begin{matrix} \text{orthosilicic} \\ \text{acid.} \end{matrix}$$
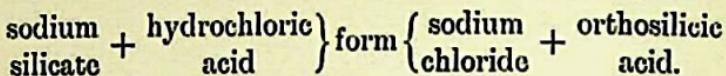
The sodium chloride is removed from the colloid solution of silicic acid by dialysis (see p. 240). Gelatinous silicic acid is precipitated if the solution of sodium silicate is too concentrated. Gelatinous silicic acid is soluble in dilute caustic soda or sodium carbonate.

We are not able to distinguish between the different varieties of silicic acid by chemical reactions such as were employed in the case of the phosphoric acids (see p. 232).

The existence of the acids is inferred from the occurrence of the salts called silicates, many of which are found in nature.

All silicates, except those of sodium and potassium, are insoluble in water. The soluble silicates are known as "water-glass". "Water-glass" may be prepared by fusing together sodium carbonate and silica.

Occurrence.—Silicic acid and sodium silicate occur in solution in the Great Geyser of Iceland, the hot springs of New Zealand, the Mammoth Hot Springs of the Yellowstone Park (U.S.A.), and other places. In some cases the silicic acid is deposited, loses water, and forms silica. The "terraces" which surround some of these hot springs are formed by the action of carbon dioxide upon the sodium and potassium silicates.

Quartz sand is formed by the action of carbonic acid upon granite, a mineral which contains silica. The grains of silica (sand) set free in this way may later get bound together by means of lime or iron oxide. In this way, sandstone is formed.

Uses.—Silica and the silicates are put to many uses. *Sandstone* is largely used as building-stone. Builders' *mortar* is a mixture of slaked lime, sand, and water. *Clay* is mainly

aluminium silicate.   Glass is a mixture of various silicates, of which the most important are sodium, potassium, and calcium silicates.   It is made by fusing quartz with the carbonates of the metals mentioned.   *Rock crystal* is used in the manufacture of spectacle lenses and in the construction of optical instruments.

Fused silica is used in the construction of glass-ware, which is subjected to great changes of temperature.   The coefficient of expansion of fused silica is so small that a red-hot silica vessel may be placed in cold water without sustaining a fracture.

Water-glass (sodium silicate) is largely used for preserving eggs.

SILICON

The element silicon exists in several forms.   By heating finely powdered quartz with magnesium powder an amorphous form of silicon is obtained.[1]

$$\left.\begin{array}{l} \text{silicon} \\ \text{dioxide} \end{array} + \text{magnesium}\right\} \text{form} \left\{\begin{array}{l} \text{magnesium} \\ \text{oxide} \end{array} + \text{silicon}.\right.$$
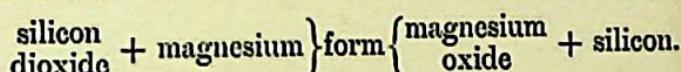
The magnesium oxide produced is dissolved out by means of dilute acid, which does not affect the silicon.

If amorphous silicon be dissolved in molten aluminium, the silicon on cooling assumes the crystalline form.

Crystalline silicon is not affected by heat, but the amorphous variety can be ignited.   As it burns it becomes coated with a layer of silica which prevents further combustion.

Silicon is soluble in caustic soda, forming sodium silicate. Hydrogen is evolved.   Silicon burns in chlorine to form silicon tetrachloride.

History.—The manufacture of glass from silicates has been known from ancient times.   The presence of what we now call "silica" was recognized in these silicates in the seventeenth century.   It was next noticed that the silica had to be

[1] This reaction is apt to take place with explosive violence, and is consequently unsuitable for class demonstration.

mixed with other materials, such as soda or potash, before it would fuse. In 1773 Scheele demonstrated the acid character of silica. The search for the element of which silica is the oxide was then undertaken. In 1823 Berzelius succeeded in preparing silicon in the amorphous condition.

CHAPTER XXII

CHARACTERISTICS OF THE METALS

We have already arranged the elements in two groups— metals and non-metals—according to their chemical behaviour (see p. 52).

The chemical behaviour of their oxides is perhaps the best test as to whether an element is to be classed as a metal or a non-metal, but even when judged by *this* test the dividing line is not the hard-and-fast line we have so far considered it to be. For example, the element chromium forms both an acid oxide (from which the salts called chromates are formed) and also a basic oxide (from which the chromium salts like chromium chloride are formed).

Similarly with manganese, which acts chemically as a non-metal in manganates or permanganates, but acts as a metal in manganese salts.

It is worth while, therefore, to consider the physical properties (see p. 101) which are generally associated with the word *metal*. For this purpose we will compare the physical properties of some common metals and non-metals.

Experiment 136.—To compare some of the physical properties of the metals lead, iron, copper, and zinc with those of the non-metals carbon, sulphur, phosphorus, and iodine.

Examine specimens of each of the elements named above, with a view to answering the questions set out below. Tabulate your answers as follows:—

Is the element—	NON-METALS.				METALS.			
	Carbon.	Iodine.	Sulphur.	Phosphorus	Lead.	Iron.	Copper.	Zinc.
i. Opaque or transparent? ...								
ii. Malleable or brittle? ...								
iii. Ductile[1] or not?[2] ...								
iv. A good or bad conductor of heat and electricity?[3]								
v. One with a high or a low boiling-point?[2]								
vi. One possessing a metallic lustre?							•	

It will be seen from the results of Experiment 136 that metals are distinguishable to a large extent from non-metals by their physical properties.

There are exceptions, however. Iodine and graphite possess the metallic lustre of the metals. Graphite is also a fairly good conductor of electricity. Carbon and sulphur are opaque, but then, again, metals are transparent if in very thin sheets. For example, gold-leaf is transparent to green light.

In deciding whether to class an element as a metal or a non-metal we must take into account its physical and chemical properties.

Metals generally—

(i) Possess a metallic lustre.

(ii) Are opaque, malleable, and ductile.

(iii) Are good conductors of heat and electricity.

[1] Ductile means capable of being drawn out into wire.

[2] Refer to your textbook for this information.

[3] Insert a specimen of each element (except phosphorus) in an electric circuit, say that of an electric pocket-lamp. With good conductors the light will be almost as bright as before the insertion of the element in the circuit.

(iv) Have a high density.

(v) Are soluble in acids.

(vi) Do not form hydrides, that is, compounds with hydrogen.

(vii) Are electro-positive (see pp. 68 and 278).

We shall next study some of the common metals and their more important compounds. In doing so, where there is a similarity between the metallic elements and their corresponding compounds they will be considered together. In this way we may hope to bring into greater prominence this similarity. The student is again advised that it will help him to understand the different reactions discussed if he will endeavour—

(i) Wherever possible to view the reactions as double decompositions (see p. 112).

(ii) To consider a solution of carbon dioxide in water as carbonic acid.

(iii) To consider a solution of sulphur dioxide in water as sulphurous acid.

(iv) To think of the acids as hydrogen salts; for example, of hydrochloric acid as hydrogen chloride, of sulphuric acid as hydrogen sulphate.

CHAPTER XXIII

SODIUM AND POTASSIUM

Sodium.—*Occurrence.*—Sodium occurs naturally only in compounds. The chief sources of supply of sodium compounds are—

(i) Common salt (sodium chloride), which occurs in sea-water and in the rock-salt deposits of Cheshire, Wielicza (near Cracow), and many other places.

(ii) Sodium nitrate (Chili saltpetre), which occurs in South America.

Production.—The metal was discovered by Davy, who obtained it by passing a current of electricity through some solid caustic soda which had been exposed to the air just long enough to become moist but not wet. The moisture was then just sufficient to make the substance a conductor of electricity, but not enough to convert the sodium into sodium hydroxide as quickly as it was formed. In previous attempts to decompose sodium hydroxide in solution by means of electricity, the sodium decomposed the water as soon as it was liberated. The result was that hydrogen and sodium hydroxide were obtained (see p. 58). Salts of sodium behave in a similar manner on electrolysis.[1]

For example:

		At the Anode.	At the Cathode.
sodium hydroxide (solution)	on electrolysis forms }	oxygen	{ sodium hydroxide + hydrogen.
sodium chloride (solution)	" " " }	chlorine	{ sodium hydroxide + hydrogen.
sodium hydroxide (melted)	" " " }	oxygen	sodium.

Sodium is prepared commercially by a process somewhat similar to that of Davy, except that the caustic soda is rendered conductive by fusion.

Potassium. — *Occurrence.*—Like sodium, potassium occurs naturally only in compounds. The chief compounds are:

(i) In rocks as potassium aluminium silicate.

(ii) In the Stassfurt deposits as potassium chloride.

Production.—The metal was discovered by Davy in 1807 in a manner similar to that by which he first obtained sodium. The same difficulty in decomposing caustic potash (potassium hydroxide) was met with as occurs in the case of caustic soda.

[1] For an explanation of the electrical terms used in this chapter see Chapter XLVI, *A Course in Physics*, published by Messrs. Blackie & Son.

The metal is prepared commercially by the electrolysis of fused caustic potash, and in other ways.

Properties:

	Sodium.	Potassium.
Hardness ...	Soft; easily cut with a knife.	The same.
Malleability ...	Easily moulded between the fingers.	The same.
Colour	Silvery lustre when freshly cut but rapidly tarnishes—that is, becomes coated with a layer of oxide—when exposed to the air.	The same, but it tarnishes more rapidly.
Melting-point ...	95·6° C.	62° C.
Boiling-point ...	877° C.	700° C.
Density ...	·97.	·87.

Both sodium and potassium burn in oxygen, forming sodium and potassium oxides (see Experiment 35 (v)). They also burn in chlorine, forming sodium and potassium chlorides (see p. 132).

Both metals decompose water at ordinary temperatures, with the evolution of hydrogen and the formation of the hydroxides of sodium and potassium (see Experiment 37). In the case of potassium the heat developed is sufficient to set fire to the hydrogen produced.

Sodium Peroxide.—When sodium burns in air or in oxygen a yellowish-white powder is formed. This is mainly sodium peroxide (see Experiment 35). If heated strongly sodium peroxide is decomposed into a lower oxide of sodium, and oxygen is given off.

sodium peroxide forms sodium oxide + oxygen.
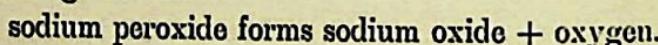
The same change is brought about by the addition of warm water[1] to the peroxide. The sodium oxide formed combines with the water to form sodium hydroxide.

$$\left. \begin{array}{c} \text{sodium} \\ \text{peroxide} \end{array} + \text{water} \right\} \text{form} \left\{ \begin{array}{c} \text{sodium} \\ \text{hydroxide} \end{array} + \text{oxygen.} \right.$$
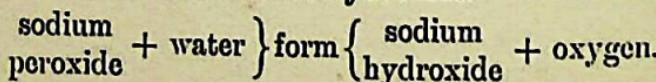
[1] With ice-cold water or acid, hydrogen peroxide—a compound of hydrogen and oxygen—is formed.

Similarly, with acids—

$$\left.\begin{matrix} \text{sodium} \\ \text{peroxide} \end{matrix}\right. + \left.\begin{matrix} \text{hydrochloric} \\ \text{acid} \end{matrix}\right\} \text{form} \left\{\begin{matrix} \text{sodium} \\ \text{chloride} \end{matrix} + \text{water} + \text{oxygen}.\right.$$
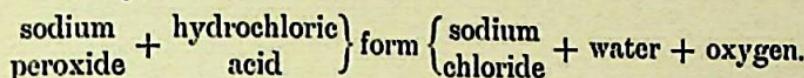
The substance is therefore a powerful oxidizing agent. As such it is largely used both in the laboratory and in everyday life. It is sold as "soda bleach".

Experiment 137.—(i) Fuse some chromium chloride with a small quantity of sodium peroxide on a piece of porcelain. Notice the change from the green chromium salt to the more highly oxidized yellow chromate.

(ii) Make a cold solution of sodium peroxide in very dilute hydrochloric acid.

- (a) Dip a piece of potassium iodide starch-paper into the solution, and notice the blue colour produced. Explain the result.
- (b) Dip a piece of litmus-paper into the solution. Notice the decolorizing effect of the solution upon the litmus. Explain the result.

(iii) Make a solution of sodium sulphite. To a little of the solution add concentrated hydrochloric acid. Notice the smell of the sulphur dioxide evolved. This is a convenient test for a sulphite.

To a further quantity of the solution of sodium sulphite add a little sodium peroxide. Add concentrated hydrochloric acid to the solution, and notice that sulphur dioxide is not now given off. To the solution add barium chloride. Notice the white precipitate which falls, indicating the presence of a *sulphate*.

The sodium sulphite has been oxidized to sodium sulphate.

(iv) Similarly, the solution of sodium peroxide may be used to oxidize (a) a ferrous salt to a ferric salt; (b) lead sulphide to lead sulphate.

Potassium Peroxide.—Potassium peroxide is prepared by heating potassium in dry air or oxygen. Like sodium peroxide it is a white powder, with powerful oxidizing properties. On prolonged heating it unites with more oxygen from the air,

forming a still higher oxide of potassium. In this respect it differs from sodium peroxide.

Sodium Hydroxide (caustic soda) may be formed by dissolving sodium peroxide in water. The usual method of preparation, however, is to act upon sodium carbonate with lime.

$$\left.\begin{array}{c}\text{sodium}\\ \text{carbonate}\end{array} + \begin{array}{c}\text{calcium}\\ \text{oxide.}\end{array} + \text{water}\right\}\text{form}\left\{\begin{array}{c}\text{calcium}\\ \text{carbonate}\end{array} + \begin{array}{c}\text{sodium}\\ \text{hydroxide.}\end{array}\right.$$
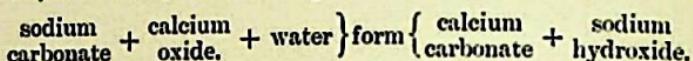
Experiment 138.—Make a concentrated solution of sodium carbonate in a beaker. Add lime to the solution and notice the precipitate of calcium carbonate which forms. Boil the solution and continue the addition of the lime until on withdrawing a small quantity of the solution and adding hydrochloric acid to it no effervescence takes place. The whole of the carbonate has then been precipitated. Decant the clear solution, which contains the caustic soda. The liquid may be evaporated to dryness in a nickel or iron crucible (why not glass or glazed porcelain? see p. 247) and solid caustic soda is obtained.

Caustic soda is prepared commercially by a method similar to the above. It is also prepared by the electrolysis of a solution of common salt (see p. 251).

It is a white, deliquescent, amorphous solid. It exerts a very corrosive action on plant and animal tissue. The solid is very soluble in water and rapidly absorbs carbon dioxide, forming sodium carbonate, and ultimately sodium bicarbonate.

$$\left.\begin{array}{c}\text{sodium}\\ \text{hydroxide}\end{array} + \begin{array}{c}\text{carbon}\\ \text{dioxide}\end{array}\right\}\text{form}\left\{\begin{array}{c}\text{sodium}\\ \text{carbonate}\end{array} + \text{water.}\right.$$
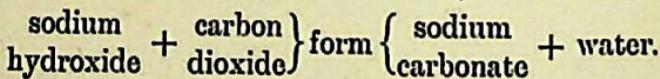
Experiment 139.—Make a solution of caustic soda in a test-tube. Pass a current of carbon dioxide through the solution for a few minutes.

Examine the solution for the presence of a carbonate by adding hydrochloric acid to the solution.

Caustic soda is used in the laboratory to remove carbon dioxide from gases, and in the arts in the manufacture of soap and paper.

fat + caustic soda form soap + glycerine.
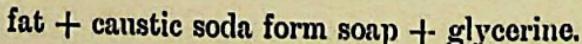
Potassium Hydroxide (caustic potash) is prepared similarly to caustic soda. Lime is added to a solution of potassium carbonate until the liquid does not effervesce with dilute acid. The liquid is then concentrated in iron pans and finally in silver ones until, on cooling, it solidifies. The solid is brittle and deliquescent. It is very soluble in water, and exerts a corrosive action on plant and animal tissue. Like caustic soda it absorbs—

(i) Carbon dioxide, forming potassium bicarbonate.
(ii) Sulphur dioxide, forming potassium bisulphite.
(iii) Hydrogen sulphide, forming acid potassium sulphide.
(iv) Chlorine, forming potassium chloride (and potassium chlorate if the solution is warm).

When neutralized by the halogen acids (hydrochloric acid, hydrobromic acid, and hydriodic acid), potassium chloride, potassium bromide, and potassium iodide respectively are formed. Caustic potash is used in the manufacture of "soft soap".

Sodium Chloride (common salt), as already mentioned (p. 250), occurs naturally in large quantities. It is obtained from the mines of Cheshire by dissolving it in water while it is in the ground and pumping up the brine. The brine is then evaporated to recover the salt. In warm countries it is obtained from sea-water by evaporation from shallow pools.

Sodium chloride consists of cubical white crystals containing no water of crystallization. It is used in large quantities in the manufacture of sodium sulphate (see p. 259), washing-soda (see p. 256), and caustic soda (see p. 254). It is also employed in glazing pottery. England alone produces 2,000,000 tons of salt yearly.

Pure sodium chloride is not deliquescent. Salt used for domestic purposes becomes damp on exposure to the air because of the deliquescent impurities—for example, magnesium chloride—which it contains.

Potassium Chloride.—The chief source of supply of this salt

is the Stassfurt deposits. It is found at Stassfurt as a compound of potassium chloride and magnesium chloride (a double salt). The potassium chloride, being less soluble than the magnesium chloride, is separated from the solution by fractional crystallization (see p. 237). Like sodium chloride, potassium chloride crystallizes in white cubical crystals.

Sodium Carbonate (washing-soda) and **sodium bicarbonate** (baking-soda).—Sodium carbonate is manufactured on a very
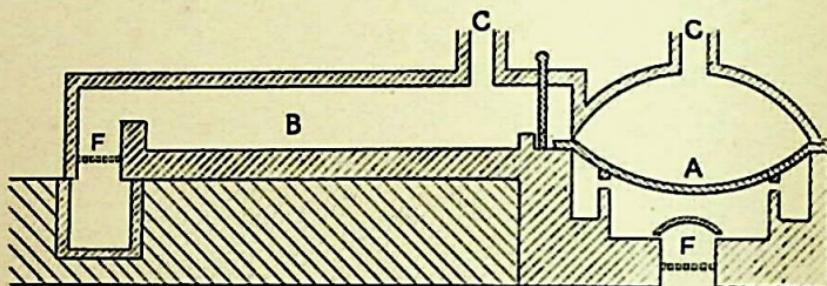
Fig. 110.—Manufacture of Washing-soda

A, Cast-iron pan in which common salt is converted into acid sodium sulphate. B, Reverberatory furnace in which acid sodium sulphate is converted into normal sodium sulphate. C, C, Chimneys for the escape of hydrochloric acid gas. F, F, Furnace fires.

large scale. In Great Britain alone about 1,000,000 tons are produced annually.

When caustic soda is saturated with carbon dioxide, sodium bicarbonate is formed. If to the solution a volume of caustic soda equal to that originally used be added, the normal salt is obtained.

$$\left.\begin{array}{c}\text{sodium}\\\text{hydroxide}\end{array} + \begin{array}{c}\text{carbon}\\\text{dioxide}\end{array}\right\}\text{form}\left\{\begin{array}{c}\text{sodium}\\\text{bicarbonate.}\end{array}\right.$$

$$\left.\begin{array}{c}\text{sodium}\\\text{hydroxide}\end{array} + \begin{array}{c}\text{sodium}\\\text{bicarbonate}\end{array}\right\}\text{form}\left\{\begin{array}{c}\text{sodium}\\\text{carbonate.}\end{array}\right.$$
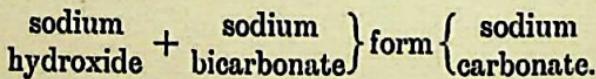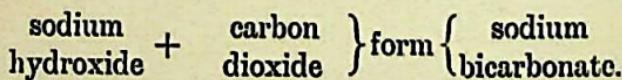
Sodium carbonate was largely obtained from the ashes of sea-weeds prior to 1790. Leblanc, a French chemist, about that time devised a method which, in spite of a cheaper process —the Solvay process—is still in use.

I. *The Leblanc Process.*—This process occurs in three stages.

(i) Common salt is converted into sodium sulphate by means of sulphuric acid. The reaction takes place in two steps, and in each of them hydrochloric acid is evolved, and forms a valuable by-product. The common salt and sulphuric acid are roasted at a gentle heat in cast-iron pans (A, fig. 110).

$$\left.\begin{array}{c}\text{sodium}\\\text{chloride}\end{array} + \begin{array}{c}\text{sulphuric}\\\text{acid}\end{array}\right\} \text{form} \left\{\begin{array}{c}\text{sodium hydrogen}\\\text{sulphate}\end{array} + \begin{array}{c}\text{hydrochloric}\\\text{acid.}\end{array}\right.$$
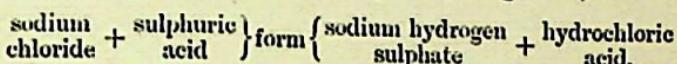
The sodium hydrogen sulphate is then raked out of the pan on to the bed (B) of a reverberatory furnace, that is, a furnace in which the flame reverberates or passes from side to side. Here the reaction is completed, for at the higher temperature of this furnace—

$$\left.\begin{array}{c}\text{sodium hydrogen}\\\text{sulphate}\end{array} + \begin{array}{c}\text{sodium}\\\text{chloride}\end{array}\right\} \text{form} \left\{\begin{array}{c}\text{sodium}\\\text{sulphate}\end{array} + \begin{array}{c}\text{hydrochloric}\\\text{acid.}\end{array}\right.$$
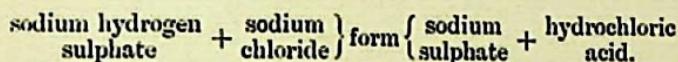
(ii) The sodium sulphate (salt cake) is roasted with lime-stone and coal. The carbon of the coal reduces the sodium sulphate to sodium sulphide.

$$\left.\begin{array}{c}\text{sodium}\\\text{sulphate}\end{array} + \text{carbon}\right\} \text{form} \left\{\begin{array}{c}\text{sodium}\\\text{sulphide}\end{array} + \begin{array}{c}\text{carbon}\\\text{monoxide.}\end{array}\right.$$
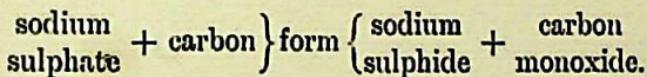
The sodium sulphide and the limestone then suffer double decomposition. The roasted mass is called "black ash".

$$\left.\begin{array}{c}\text{sodium}\\\text{sulphide}\end{array} + \begin{array}{c}\text{calcium}\\\text{carbonate}\end{array}\right\} \text{form} \left\{\begin{array}{c}\text{sodium}\\\text{carbonate}\end{array} + \begin{array}{c}\text{calcium}\\\text{sulphide.}\end{array}\right.$$
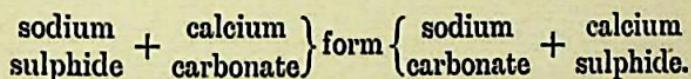
(iii) The "black ash" is then extracted with water, which dissolves the sodium carbonate (and other substances). The solution is evaporated to dryness, and the impure soda thus obtained is dissolved in water from which it crystallizes as "washing-soda".

There are many valuable by-products of this process. Hydrochloric acid has already been mentioned. Much of the hydrochloric acid is converted into chlorine (see p. 130), which is absorbed by lime to form bleaching-powder (see p. 132).

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The sulphur is also extracted from the sulphides, and used in the manufacture of sulphuric acid, large quantities of which are required in an earlier stage (see (i) above).

II. *The Solvay or Ammonia-soda Process.*—A saturated solution of common salt (brine) is saturated with ammonia.

Carbon dioxide is then passed through the solution. Crystals of sodium bicarbonate separate out.

$$\text{ammonia} + \begin{array}{c}\text{carbon}\\\text{dioxide}\end{array} + \begin{array}{c}\text{sodium}\\\text{chloride}\end{array} \Big\} \text{form} \Big\{ \begin{array}{c}\text{sodium}\\\text{bicarbonate}\end{array} + \begin{array}{c}\text{ammonium}\\\text{chloride.}\end{array}$$
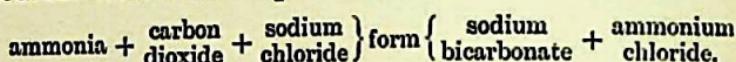
On heating, the bicarbonate is converted into the normal carbonate.

$$\begin{array}{c}\text{sodium}\\\text{bicarbonate}\end{array} \Big\} \text{forms} \Big\{ \begin{array}{c}\text{sodium}\\\text{carbonate}\end{array} + \text{water} + \begin{array}{c}\text{carbon}\\\text{dioxide.}\end{array}$$
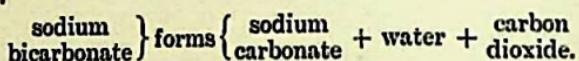
The ammonium chloride in solution is then treated with lime to recover the ammonia, which is used again.

$$\begin{array}{c}\text{calcium}\\\text{oxide}\end{array} + \begin{array}{c}\text{ammonium}\\\text{chloride}\end{array} \Big\} \text{form} \Big\{ \text{ammonia} + \text{water} + \begin{array}{c}\text{calcium}\\\text{chloride.}\end{array}$$
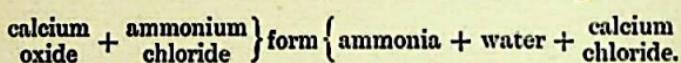
The lime and carbon dioxide required for the manufacture are obtained by heating limestone in kilns (see p. 265).

Sodium carbonate crystallizes in large transparent crystals containing water of crystallization. They effloresce in dry air. The salt is very soluble in water and the solution has an alkaline reaction. It is often found that the normal salt formed by the union of a weak acid and a strong base gives an alkaline solution.

Sodium carbonate does not decompose on being heated to redness. Sodium bicarbonate on being heated does decompose (see above). "Baking-powder" is largely composed of sodium bicarbonate. The carbon dioxide evolved during baking makes cakes "light".

Potassium carbonate is manufactured by the Leblanc process from potassium sulphate.

Potassium carbonate cannot be prepared by the Solvay process because potassium bicarbonate is soluble in water.

Just as sodium carbonate was obtained from the ash of sea plants, so potassium carbonate was, and is, obtained by burning

land plants in iron "pots". The ashes which remain contain about 30 per cent of potassium carbonate (pot-ashes).

Potassium carbonate is not decomposed even if heated to redness. It is soluble in water and forms an alkaline solution.

Potassium bicarbonate can be prepared by passing carbon dioxide through a solution of the normal carbonate. On being heated the bicarbonate yields carbon dioxide and the normal carbonate.

Sodium Sulphate.—The acid salt is formed in the preparation of hydrochloric acid and nitric acid (see pp. 125 and 141). At the higher temperature of the furnaces in which the manufacture of these substances is carried out, the normal salt is formed.

Sodium sulphate crystallizes in colourless transparent prisms which contain water of crystallization. These crystals are known as Glauber's salt. When exposed to the air the crystals effloresce and form a white anhydrous powder.

Experiment 140.—Prepare crystals of sodium sulphate by neutralizing sulphuric acid by means of sodium carbonate and concentrating the solution.

Potassium Sulphate.—The Stassfurt deposits form the main source of supply of potassium sulphate. The salt is used in the manufacture of potassium carbonate and also in agriculture. The mineral "kainit" consists of potassium sulphate, magnesium sulphate, and magnesium chloride. The potassium sulphate is obtained from the kainit by means of fractional crystallization.

Potassium sulphate is also formed by the action of sulphuric acid upon potassium chloride or potassium nitrate. Compare this with the formation of sodium sulphate. The acid potassium sulphate is first formed just as the acid sodium sulphate is formed with sodium salts (see above).

Sodium Nitrate (Chili saltpetre).—This salt occurs naturally in Chili, Peru, and Bolivia.

Prepare sodium nitrate by neutralizing nitric acid by

means of sodium carbonate. Concentrate the solution in an evaporating-dish until, on cooling, crystals are deposited.

$$\left.\begin{array}{l}\text{sodium}\\\text{carbonate}\end{array}\right\} + \left.\begin{array}{l}\text{nitric}\\\text{acid}\end{array}\right\} \text{form} \left\{\begin{array}{l}\text{sodium}\\\text{nitrate}\end{array} + \text{water} + \begin{array}{l}\text{carbon}\\\text{dioxide.}\end{array}\right.$$
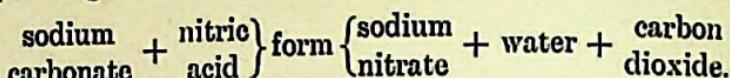
Heat a little of the sodium nitrate thus prepared in a test-tube. Is oxygen evolved? Is any other gas set free?

Sodium nitrate crystallizes without water of crystallization. The crystals are deliquescent, and for this reason cannot be employed in place of potassium nitrate in the preparation of gunpowder. Sodium nitrate is very soluble in water. Heat decomposes the salt with the evolution of oxygen, nitrogen, and oxides of nitrogen.

Sodium nitrate is largely used both as a manure and in the manufacture of nitric acid (see pp. 143 and 141).

Potassium Nitrate (saltpetre).—This salt occurs naturally on the soil in parts of India and Persia.

It is formed when nitric acid is neturalized by means of potassium carbonate or caustic potash.

$$\left.\begin{array}{l}\text{potassium}\\\text{carbonate}\end{array}\right\} + \left.\begin{array}{l}\text{nitric}\\\text{acid}\end{array}\right\} \text{form} \left\{\begin{array}{l}\text{potassium}\\\text{nitrate}\end{array} + \text{water} + \begin{array}{l}\text{carbon}\\\text{dioxide.}\end{array}\right.$$
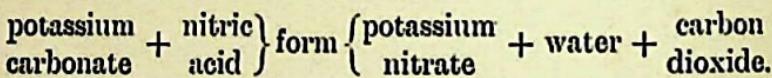
Potassium nitrate is prepared from sodium nitrate and potassium chloride by double decomposition. The mixture is boiled and the less-soluble sodium chloride crystallizes out from the hot solution. The potassium nitrate crystallizes out on cooling.

Potassium nitrate crystallizes without water of crystallization, and the crystals, unlike those of sodium nitrate, are not deliquescent. They are very soluble in water. Heat decomposes the salt with the evolution of oxygen.

$$\left.\begin{array}{l}\text{potassium}\\\text{nitrate}\end{array}\right\} \text{forms} \left\{\begin{array}{l}\text{potassium}\\\text{nitrite}\end{array} + \text{oxygen.}\right.$$
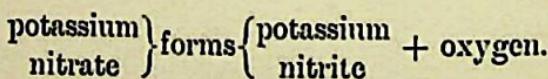
Potassium nitrate is therefore a strong oxidizing agent. For example, when the salt is heated strongly with—

(a) *Powdered carbon*, a violent deflagration takes place and the carbon is oxidized to carbon dioxide.

$$\left.\begin{matrix} \text{potassium} \\ \text{nitrate} \end{matrix} + \text{carbon} \right\} \text{form} \left\{ \begin{matrix} \text{potassium} \\ \text{carbonate} \end{matrix} + \begin{matrix} \text{carbon} \\ \text{dioxide} \end{matrix} + \text{nitrogen (i)} \right.$$
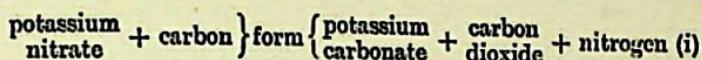
(b) *Sulphur*, the sulphur is oxidized to sulphur dioxide.

$$\left.\begin{matrix} \text{potassium} \\ \text{nitrate} \end{matrix} + \text{sulphur} \right\} \text{form} \left\{ \begin{matrix} \text{potassium} \\ \text{sulphate} \end{matrix} + \begin{matrix} \text{sulphur} \\ \text{dioxide} \end{matrix} + \text{nitrogen (ii)} \right.$$
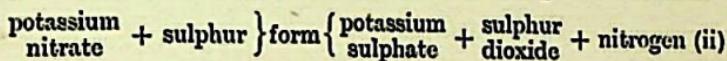
Potassium nitrate is used in the manufacture of gunpowder, which is a mixture of (about) 75 per cent potassium nitrate, 10 per cent sulphur, and 15 per cent carbon. When the gunpowder is ignited the potassium nitrate supplies the oxygen required to oxidize the sulphur and carbon to sulphur dioxide and carbon dioxide respectively (see (i) and (ii) above). When the combustion takes place in a closed space, the great pressure exerted is due to the fact that large quantities of hot gases are evolved.

Sodium Sulphite.—There are two sodium salts of sulphurous acid—the normal salt and the acid salt (see pp. 170 and 92). The acid salt is formed in solution when caustic soda solution is saturated with sulphur dioxide. On adding a volume of caustic soda equal to that originally employed, to the solution saturated with sulphur dioxide, the normal salt is obtained in solution. To obtain the solids the water in the solutions must be allowed to evaporate at ordinary temperature. If the solutions are boiled the sulphites will be oxidized by the air to sulphates.

$$\left.\begin{matrix} \text{sodium} \\ \text{hydroxide} \end{matrix} + \begin{matrix} \text{sulphur} \\ \text{dioxide} \end{matrix} \right\} \text{form} \left\{ \begin{matrix} \text{sodium} \\ \text{bisulphite} \end{matrix} + \text{water.} \right.$$

$$\left.\begin{matrix} \text{sodium} \\ \text{bisulphite} \end{matrix} + \begin{matrix} \text{sodium} \\ \text{hydroxide} \end{matrix} \right\} \text{form} \left\{ \begin{matrix} \text{sodium} \\ \text{sulphite} \end{matrix} + \text{water.} \right.$$
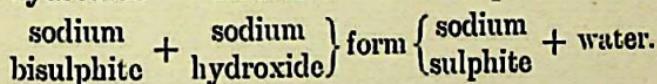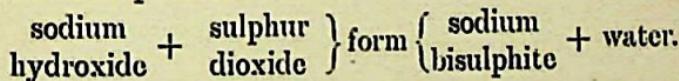
Because of the ease with which sodium sulphite is oxidized to sodium sulphate it is a powerful reducing agent. For example, it is used to remove the unused chlorine from articles after bleaching. The following reaction then occurs:—

$$\text{chlorine} + \text{water} + \left.\begin{matrix} \text{sodium} \\ \text{sulphite} \end{matrix} \right\} \text{form} \left\{ \begin{matrix} \text{hydrochloric} \\ \text{acid} \end{matrix} + \begin{matrix} \text{sodium} \\ \text{sulphate.} \end{matrix} \right.$$
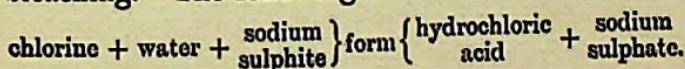
The chlorine combines with the hydrogen of the water present, and the sulphite combines with the oxygen of the water.

Sodium sulphite dissolves sulphur, forming sodium thiosulphate (see below).

Hydrochloric acid decomposes sodium sulphite, with the evolution of sulphur dioxide.

$$\left.\begin{array}{c}\text{sodium}\\\text{sulphite}\end{array}+\begin{array}{c}\text{hydrochloric}\\\text{acid}\end{array}\right\}\text{form}\left\{\begin{array}{c}\text{sodium}\\\text{chloride}\end{array}+\begin{array}{c}\text{sulphur}\\\text{dioxide.}\end{array}\right.$$
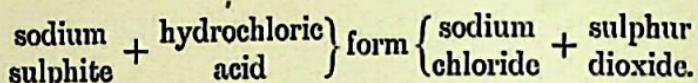
Experiment 141.—To prepare sodium bisulphite and sodium sulphite.

Pass sulphur dioxide into a measured volume of caustic soda solution until no more sulphur dioxide will dissolve. The acid sodium sulphite is formed. Do not concentrate the solution by boiling.

(i) Place half the solution in a crystallizing-dish and set it aside for a few days, when crystals of sodium bisulphite will be deposited.

(ii) To the other half of the solution of sodium bisulphite add an equal volume of the caustic soda solution. On standing for some days the mixture will deposit crystals of normal sodium sulphite.

Sodium Thiosulphate.—When sulphur is dissolved in sodium sulphite, sodium thiosulphate is formed. Sulphur, in this case, oxidizes the sulphite into thiosulphate, just as oxygen will oxidize the sulphite into sulphate on boiling.

Sodium thiosulphate is used by photographers for " fixing " plates and prints, that is, rendering them insensitive to the action of light. The salt on the plate which would be acted upon by the light is generally silver chloride or bromide. Sodium thiosulphate acts upon the *silver* chloride forming *sodium* chloride. The displaced silver takes the place of the sodium in the sodium thiosulphate and forms a soluble salt. Thus in place of the insoluble silver chloride two soluble salts are formed.

Hydrochloric acid decomposes sodium thiosulphate, forming sodium chloride and sulphur.

hydro-
chloric + sodium
thio- } form { sodium + sulphur + sulphur + water.
acid sulphate } chloride dioxide
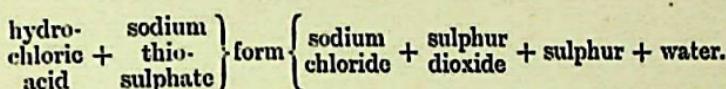
Experiment 142.—Make a warm saturated solution of sodium sulphite in a beaker. Add flowers of sulphur to the solution until no more will dissolve. Filter the solution to remove the excess of sulphur and place the filtrate aside to crystallize. To one or two of the crystals in a test-tube add a little dilute hydrochloric acid. Notice the precipitate of sulphur which forms and the smell of sulphur dioxide evolved.

Potassium Permanganate.—Fuse together in a crucible about equal weights of manganese dioxide, potassium chlorate, and caustic potash. Allow the fused mass to cool and then boil it with water. A purple solution containing potassium permanganate is obtained. Allow the liquid to stand for a few minutes and then decant the clear liquid. Concentrate the purple solution so obtained, until, on cooling, crystals of potassium permanganate are obtained.

Potassium permanganate crystals are almost black and have a metallic lustre. They dissolve in water, forming a deep-purple solution. The solution is a strong oxidizing agent, as also is the solid. For example, sulphur, carbon, or phosphorus are oxidized by solid potassium permanganate with explosive violence. Glycerine—a compound of carbon, hydrogen, and oxygen—takes fire on the addition to it of solid potassium permanganate.

The oxidizing property of potassium permanganate may be shown by using a solution of the salt to—(i) Oxidize a ferrous salt in the presence of sulphuric acid to a ferric salt. (ii) Oxidize sulphurous acid to sulphuric acid.

In each case the purple colour of the permanganate solution is destroyed.

The use of potassium permanganate as a disinfectant is due to its oxidizing properties.

QUESTIONS ON CHAPTER XXIII

1. How would you distinguish, by experiment, between sodium carbonate and sodium hydrogen carbonate?

2. How would you prepare a pure specimen of potassium nitrate, if you were provided with aqueous solutions of calcium nitrate and potassium sulphate?

3. State the principal chemical changes which occur in the manufacture (a) of sodium carbonate from common salt, (b) of caustic soda from sodium carbonate. Give also a sketch of the processes of manufacture. (C. L.)

4. How is sodium prepared commercially? Describe the preparation, properties, and uses of three compounds of this metal.

5. Describe briefly the manufacture of washing-soda and of sodium bicarbonate from common salt.

6. How may sodium hydroxide be prepared? How does sodium hydroxide react chemically with (a) nitric acid, (b) carbon dioxide, (c) sulphuric acid, (d) a solution of mercuric chloride? (C. L.)

CHAPTER XXIV

CALCIUM

Occurrence and Production.—Calcium, like sodium and potassium, is never found in nature in the uncombined state. It occurs extensively (i) as calcium carbonate in the minerals limestone, chalk, and marble; (ii) as calcium sulphate in gypsum; and (iii) as calcium phosphate in the mineral apatite.

The metal was first obtained by Davy in 1808. Davy's success in decomposing a salt of calcium and obtaining the metal was due to the fact that he used a current of electricity to effect the decomposition (see also Sodium and Potassium).

Calcium is now manufactured by the electrolysis of fused calcium chloride.

Properties.—

Hardness ...	{ Not so soft as sodium. { Easily cut and filed.
Malleability ...	Can be hammered into sheets.
Colour	Bright yellowish surface when freshly cut.
Density	1·58.

Calcium decomposes water at ordinary temperatures with the liberation of hydrogen (see p. 58). It also burns if heated in air or oxygen, forming calcium oxide (lime).
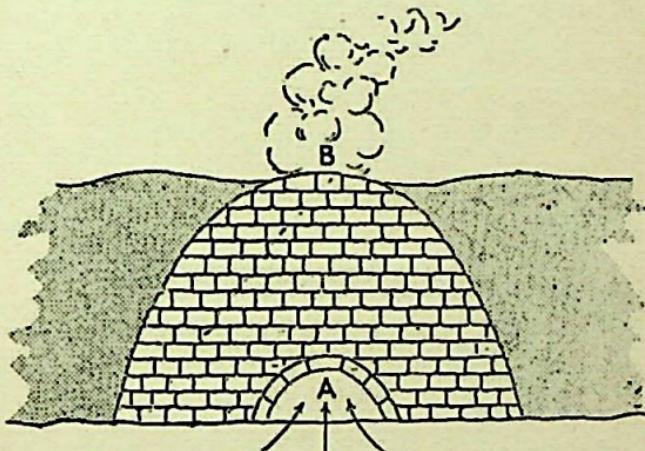

Fig. 111.—Lime Kiln

The kiln contains loosely-packed limestone and coal. Air enters at A. Carbon dioxide leaves at B.

Calcium Oxide (quicklime).—Calcium oxide is made in large quantities, for building and other purposes, from calcium carbonate (limestone). The limestone, mixed with coal, is burned in a lime-kiln (fig. 111).

Lime, or quicklime as it is called, unites with water to form a white powder called "slaked lime", with the evolution of much heat (see p. 96). Dry slaked lime will absorb chlorine, and is used commercially as a means of storing chlorine for

bleaching purposes. Lime saturated with chlorine is sold as *bleaching-powder*, and is largely used by manufacturers to bleach cotton and linen goods and paper.

The articles to be bleached are first soaked in a solution of bleaching-powder, and then in a dilute solution of hydrochloric acid. The acid liberates the chlorine from its combination with the lime, with the result that the article is bleached (see p. 132).

Lime is not fusible unless heated to above 3000° C. When heated it becomes brilliantly incandescent, and is therefore used as the illuminant in "limelight" lanterns. Builders' mortar is composed of lime and sand (silica) made into a paste with water. The "setting" (hardening) of mortar is partly due to the evaporation of the water, but mainly to the absorption by the lime of carbon dioxide from the air. The lime is thus converted into limestone.

$$\left.\begin{array}{c}\text{calcium}\\\text{oxide}\end{array}\right\} + \left.\begin{array}{c}\text{carbon}\\\text{dioxide}\end{array}\right\} \text{form} \left\{\begin{array}{l}\text{calcium}\\\text{carbonate.}\end{array}\right.$$
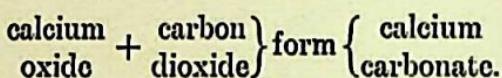
Calcium Hydroxide (slaked lime).—When water is added to lime the lime unites with the water, forming a white amorphous powder. This is calcium hydroxide.

$$\left.\begin{array}{c}\text{calcium}\\\text{oxide}\end{array}\right\} + \text{water} \left.\right\} \text{form} \left\{\begin{array}{l}\text{calcium}\\\text{hydroxide.}\end{array}\right.$$
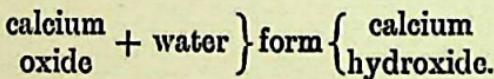
Calcium hydroxide is somewhat soluble in water, and forms an alkaline caustic solution called lime-water. Calcium hydroxide is, however, much less soluble than sodium hydroxide.

Lime-water is also formed when calcium decomposes water (see p. 58). Like caustic soda, calcium hydroxide absorbs chlorine. Provided the solution be hot, calcium chloride and calcium chlorate are formed (see p. 255).

Calcium Chloride.—This salt may be prepared by neutralizing hydrochloric acid by means of lime or calcium carbonate.

$$\left.\begin{array}{c}\text{calcium}\\\text{carbonate}\end{array}\right\} + \left.\begin{array}{c}\text{hydrochloric}\\\text{acid}\end{array}\right\} \text{form} \left\{\begin{array}{l}\text{calcium}\\\text{chloride}\end{array}\right. + \text{water} + \left.\begin{array}{c}\text{carbon}\\\text{dioxide.}\end{array}\right.$$
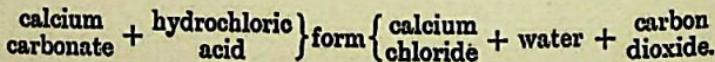
It is also obtained as a by-product in the manufacture of

sodium carbonate (see p. 258). Calcium chloride is very deliquescent, and for this reason is constantly used in the laboratory for the purpose of drying gases. It cannot, however, be used for drying ammonia gas, because the calcium chloride would absorb the ammonia, forming a compound of ammonia and calcium chloride.

Calcium chloride readily dissolves in water, and a hot solution of the salt deposits crystals of calcium chloride on cooling.

Calcium carbonate occurs naturally in the minerals limestone, chalk, and marble. It is formed when carbon dioxide is absorbed by lime or lime-water (see p. 91). The normal salt is almost insoluble in water, but dissolves in water containing carbon dioxide with the formation of the acid salt—calcium bicarbonate (see p. 91). On heating to about 600° C. calcium carbonate is decomposed, forming lime and carbon dioxide (see p. 95). In its behaviour when heated calcium carbonate differs from sodium and potassium carbonates but resembles the carbonates of the other metals.

Calcium carbonate is decomposed by dilute acids, carbon dioxide being given off (see p. 88).

Calcium sulphate occurs naturally. The mineral gypsum is calcium carbonate containing water of crystallization. On heating gypsum to 130° C. it loses three-quarters of its water of crystallization and forms a white powder called "plaster of Paris". This, when mixed into a paste with water, gradually sets into a hard mass. This is due to the fact that the plaster of Paris re-hydrates itself and changes again into gypsum. It is this property of plaster of Paris which makes it so useful in the production of mouldings and decorations.

Calcium sulphate is often found in spring water, and when present is one cause of the "permanent" hardness of the water (see p. 112).

Calcium sulphate in the hydrated condition is precipitated by adding a solution of potassium sulphate to a solution of calcium chloride.

$$\left.\begin{matrix} \text{calcium} \\ \text{chloride} \end{matrix} + \begin{matrix} \text{potassium} \\ \text{sulphate} \end{matrix}\right\} \text{form} \left\{\begin{matrix} \text{calcium} \\ \text{sulphate} \end{matrix} + \begin{matrix} \text{potassium} \\ \text{chloride.} \end{matrix}\right.$$
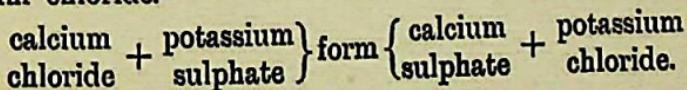
The calcium sulphate formed is almost, but not quite, insoluble in water.

Calcium Phosphate.—There are several calcium phosphates (see p. 233). The most important one, to which the name is here applied, is tri-calcium orthophosphate, which occurs in several minerals and in bone.

Calcium phosphate is almost insoluble in pure water, but dissolves in water containing other salts, such as sodium chloride, or in water containing carbon dioxide. In this way calcium phosphate in the soil finds its way into solution; otherwise it would not be absorbed by the roots of plants.

When calcium phosphate is acted upon by concentrated sulphuric acid a mixture of acid calcium phosphate, and calcium sulphate is obtained. This mixture is largely used as a manure under the name of super-phosphate of lime.

Calcium phosphate is also used in the manufacture of phosphorus (see p. 219).

QUESTIONS ON CHAPTER XXIV

1. How would you distinguish between quicklime and slaked lime?

2. What is the composition of (a) quicklime, (b) slaked lime? What chemical changes take place when slaked lime is boiled with a dilute aqueous solution of sodium carbonate? (C. L.)

3. Describe the steps you would take in order to prepare lime-water from a piece of marble. Point out carefully what chemical changes take place at each step. (C. L.)

CHAPTER XXV

ZINC AND MERCURY

Zinc.—The metal zinc has been used since the sixteenth century, when it was probably first obtained by Paracelsus. The metal is much more easily obtained from its ores than the metals sodium, potassium, and calcium are obtained from their ores. This accounts for the comparatively early discovery of zinc. Zinc can be obtained from the oxide by heating it with carbon.

Occurrence and Extraction.—The chief ores of zinc are zinc sulphide and zinc carbonate. In the extraction of zinc from its ores the ore is roasted in the presence of air. The oxide of zinc is then formed.

$$\left.\begin{matrix} \text{zinc} \\ \text{carbonate} \end{matrix}\right\} \text{forms} \left\{\begin{matrix} \text{zinc} \\ \text{oxide} \end{matrix} + \text{carbon dioxide.}\right.$$

$$\left.\begin{matrix} \text{zinc} \\ \text{sulphide} \end{matrix} + \text{oxygen}\right\} \text{form} \left\{\begin{matrix} \text{zinc} \\ \text{oxide} \end{matrix} + \begin{matrix} \text{sulphur} \\ \text{dioxide.} \end{matrix}\right.$$
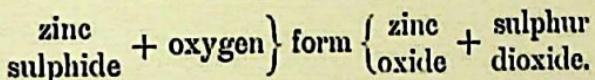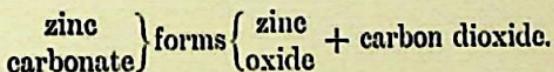
The zinc oxide is then mixed with coal and heated in retorts. The carbon reduces the zinc oxide to zinc.

$$\left.\begin{matrix} \text{zinc} \\ \text{oxide} \end{matrix} + \text{carbon}\right\} \text{form} \left\{\text{zinc} + \begin{matrix} \text{carbon} \\ \text{monoxide.} \end{matrix}\right.$$
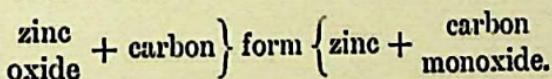
The zinc is then distilled and collected.

Properties.—Zinc is a bluish-white crystalline metal which melts at 420° C. and boils at 940° C. It has a density of 7·1. When heated above its melting-point zinc burns in the air forming zinc oxide. In moist air, at ordinary temperatures, the metal tarnishes, but the oxidation is only on the surface.

Ordinary zinc is soluble in dilute acids and also in a hot, concentrated solution of caustic soda. Hydrogen is evolved.

$$\text{zinc} + \left.\begin{matrix} \text{hydrochloric} \\ \text{acid} \end{matrix}\right\} \text{form} \left\{\begin{matrix} \text{zinc} \\ \text{chloride} \end{matrix} + \text{hydrogen.}\right.$$

$$\text{zinc} + \left.\begin{matrix} \text{sodium} \\ \text{hydroxide} \end{matrix}\right\} \text{form} \left\{\begin{matrix} \text{sodium} \\ \text{zincate} \end{matrix} + \text{hydrogen.}\right.$$
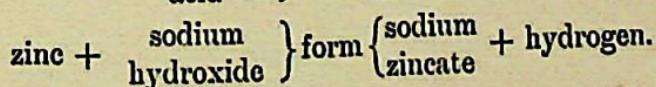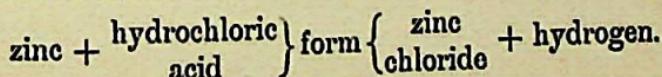
In the latter reaction, sodium is acting as the metal, and zinc as the non-metal. The salt is therefore called a zincate (see p. 248).

Ordinary zinc decomposes water at the boiling-point.

At 100° C.,

$$\text{zinc} + \text{water} \;\Big\}\; \text{form} \left\{ \begin{array}{l} \text{zinc} \\ \text{oxide} \end{array} \right. + \text{hydrogen.}$$
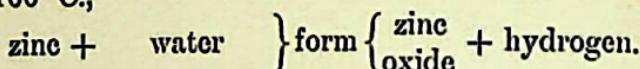
Pure zinc has no such effect upon either acid when pure, or water. The cause of the decomposition of water and acids by ordinary zinc has been shown to be due to the impurities in the zinc as much as to the zinc itself.

Zinc is used for coating sheet-iron to prevent it from rusting. Iron so treated is called galvanized iron. Zinc is also a constituent of many useful alloys (mixtures or compounds of different metals). For example—

Brass is an alloy of 2 parts of copper and 1 part of zinc.

German silver is an alloy of copper, zinc, and nickel.

Bronze coins are made of an alloy of 95 per cent of copper, 1 per cent of zinc, and 4 per cent of tin.

Zinc oxide occurs naturally as red zinc ore. It is manufactured by heating zinc above its melting-point in air. The zinc burns to zinc oxide. Zinc oxide can also be prepared by heating either zinc nitrate or zinc carbonate.

$$\left. \begin{array}{l} \text{zinc} \\ \text{carbonate} \end{array} \right\} \text{forms} \left\{ \begin{array}{l} \text{zinc} \\ \text{oxide} \end{array} \right. + \begin{array}{l} \text{carbon} \\ \text{dioxide.} \end{array}$$
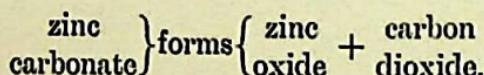
Zinc oxide is yellow when hot but white when cold. Like calcium oxide it does not fuse, even at very high temperatures, but becomes incandescent. It is insoluble in water and therefore does not form the hydroxide *directly*. It is a much weaker base than those already discussed. It is soluble in acids, however, forming zinc salts.

$$\begin{array}{l} \text{zinc} \\ \text{oxide} \end{array} + \begin{array}{l} \text{sulphuric} \\ \text{acid} \end{array} \Big\} \text{form} \left\{ \begin{array}{l} \text{zinc} \\ \text{sulphate} \end{array} \right. + \text{water.}$$
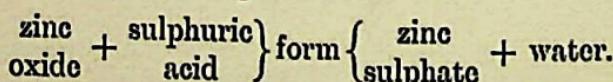
Zinc oxide is used as a pigment in place of white lead (see p. 290). It is not blackened by the sulphuretted hydrogen in

the air, as white lead is. The zinc sulphide formed when sulphuretted hydrogen attacks zinc oxide is *white*, whereas the lead sulphide formed under similar conditions is *black*.

Zinc Hydroxide.—On adding a solution of caustic soda to a solution of a soluble zinc salt a white precipitate of zinc hydroxide is formed. For example—

$$\begin{matrix} \text{zinc} \\ \text{sulphate} \end{matrix} + \begin{matrix} \text{sodium} \\ \text{hydroxide} \end{matrix} \Big\} \text{form} \Big\{ \begin{matrix} \text{zinc} \\ \text{hydroxide} \end{matrix} + \begin{matrix} \text{sodium} \\ \text{sulphate.} \end{matrix}$$
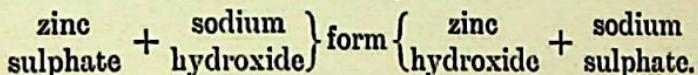
The precipitate dissolves in excess of caustic soda, forming sodium zincate. In this case the zinc oxide (a weak basic oxide) acts as an acid oxide (forming a zincate) in the presence of the strong base, caustic soda.

Similarly, when zinc dissolves in hot caustic soda, forming sodium zincate, the zinc acts as a non-metal.

Zinc sulphate is prepared commercially by roasting zinc sulphide.

$$\text{zinc sulphide} + \text{oxygen} \quad \text{form} \quad \text{zinc sulphate.}$$
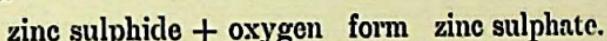
It may also be prepared by dissolving zinc, zinc oxide, or zinc carbonate in sulphuric acid.

$$\begin{matrix} \text{sulphuric} \\ \text{acid} \end{matrix} + \text{zinc} \Big\} \text{form} \Big\{ \begin{matrix} \text{zinc} \\ \text{sulphate} \end{matrix} + \text{hydrogen.}$$
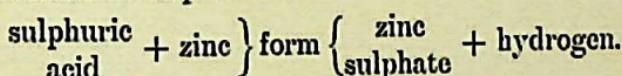
The salt crystallizes from solution in the form of colourless prisms. The crystals slowly effloresce in dry air, and are very soluble in water.

Zinc chloride is formed when zinc burns in chlorine. Commercially it is made by the action of zinc on hydrochloric acid.

It may also be prepared by the action of zinc oxide or zinc carbonate upon hydrochloric acid.

It is a soft, white, amorphous solid, which is easily fusible. It is also deliquescent, and for this reason is used as a dehydrating agent.

Zinc chloride is very soluble in water, forming a strongly caustic solution.

Zinc sulphide is a white powder. In the hydrated form zinc sulphide is precipitated as a white powder on adding

sulphuretted hydrogen to an alkaline or neutral solution of a zinc salt.

$$\left.\begin{matrix} \text{zinc} \\ \text{sulphate} \end{matrix}\right\} + \left.\begin{matrix} \text{hydrogen} \\ \text{sulphide} \end{matrix}\right\} \text{form} \left\{\begin{matrix} \text{zinc} \\ \text{sulphide} \end{matrix}\right. + \left.\begin{matrix} \text{sulphuric} \\ \text{acid.} \end{matrix}\right. \quad (i)$$
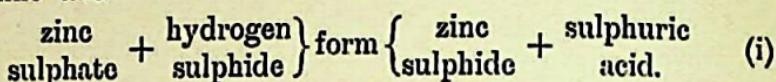
Zinc sulphide dissolves in acids with the evolution of sulphuretted hydrogen. This accounts for the necessity of having a neutral or alkaline solution of zinc sulphate in precipitating the sulphide. An alkaline solution is preferable, since the acid then formed (see (i) above) is neutralized by the alkali present.

Zinc Carbonate.—By adding potassium hydrogen carbonate to a soluble zinc salt a white precipitate of normal zinc carbonate is obtained. If normal potassium carbonate be used a basic zinc carbonate is precipitated. This tendency of zinc to form basic salts is very well marked.

MERCURY

Occurrence.—Mercury has been known from very early times. The metal was discovered early probably because it
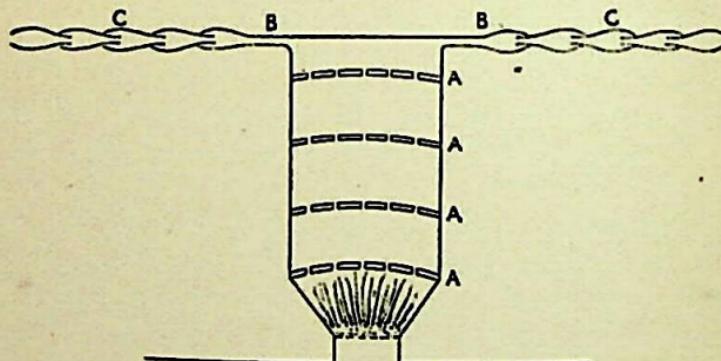
Fig. 112.—Extraction of Mercury (diagrammatic)

Mercury sulphide is placed on the shelves A. The sulphur dioxide and mercury vapour produced escape through B. The mercury is condensed in the earthenware vessels C. There are usually six rows, each containing about fifty vessels; only a few are shown.

is very easily obtained from its ore. By heating only, mercury is obtained from mercuric sulphide (cinnabar), the chief

ore of the metal. Cinnabar is mined at Almaden (Spain), Idria (Austria), and in California.

Extraction.—To obtain the metal the sulphide is roasted in a furnace (fig. 112). Sufficient air is admitted to the furnace to convert the sulphur in the mercury sulphide into sulphur dioxide.

$$\left.\begin{array}{c}\text{mercury}\\\text{sulphide}\end{array}\right. + \text{oxygen}\Big\}\text{ form }\Big\{\text{mercury} + \begin{array}{c}\text{sulphur}\\\text{dioxide.}\end{array}$$
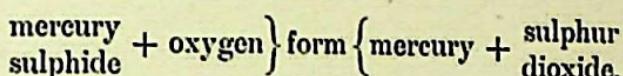
The mercury volatilizes and is condensed in suitable receivers (C, fig. 112).

Properties. —

	Mercury.	Zinc.
Melting-point ...	− 39° C.	420° C.
Boiling-point ...	360° C.	940° C.
Density	13·6	7·1
Colour	silvery-white	bluish-white.
Malleability ...	liquid	{ brittle (ductile at 150°).

Mercury does not tarnish in moist air at ordinary temperatures. Prolonged heating, however, to a temperature a little below the boiling-point of the metal, converts it into mercuric oxide (see p. 44).

Hydrochloric acid has no effect upon the metal, neither has cold sulphuric acid. Hot concentrated sulphuric acid is decomposed by mercury with the formation of mercury sulphate and sulphur dioxide.

If the mercury be in excess of the acid the mercury sulphate formed contains a higher percentage of mercury than the mercury sulphate formed when the acid is in excess. This means that there are *two* mercury sulphates. Similarly there are *two* mercury nitrates and *two* mercury chlorides. To distinguish between them, the salt with the higher percentage

of mercury is called a **mercurous** salt and the other a mercuric salt.

Dilute nitric acid dissolves mercury, forming mercurous nitrate; concentrated nitric acid is decomposed by mercury, forming mercuric nitrate and evolving oxides of nitrogen.

Mercury is attacked by chlorine, forming mercurous and mercuric chlorides.

All these salts of mercury are poisonous.

Mercury alloys with most metals, the alloys being called *amalgams*. Tin amalgam is used as a coating for mirrors.

Mercury is used in extracting silver and gold from their ores, and also as the indicating liquid in barometers and thermometers.

Mercuric oxide is formed when mercury is heated in air (see p. 44). It may also be prepared by heating mercuric nitrate or by adding caustic soda to a soluble mercury salt. For example—

$$\left.\begin{array}{c}\text{mercuric}\\\text{nitrate}\end{array} + \begin{array}{c}\text{sodium}\\\text{hydroxide}\end{array}\right\} \text{form} \left\{\begin{array}{c}\text{mercuric}\\\text{oxide}\end{array} + \begin{array}{c}\text{sodium}\\\text{nitrate}\end{array} + \text{water.}\right.$$
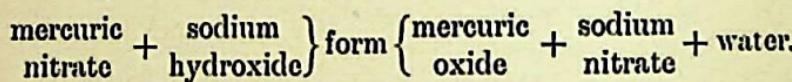
(Compare this reaction with the corresponding reaction with zinc salts, copper salts, &c.)

The precipitated mercuric oxide is in the form of a yellow powder, which on heating to 400° C. turns red. Further heating causes the red mercuric oxide to become black, and ultimately decomposes it into mercury and oxygen (see p. 43).

Mercuric oxide is slightly soluble in water, and the solution is feebly alkaline.

Mercurous nitrate is formed when mercury is dissolved in dilute nitric acid. On concentrating the solution colourless crystals are deposited. The salt is soluble in water acidified with dilute nitric acid. With pure water a white precipitate is formed. This precipitate is a basic salt—that is, a salt which contains more than the normal quantity of the base. It is called basic mercurous nitrate.

Mercuric nitrate is formed when mercury is dissolved in concentrated nitric acid. The mixture is boiled until the

liquid gives no precipitate with common salt. This indicates that there is no mercurous nitrate present.

To obtain crystals of the salt special precautions must be taken, for the crystals are deliquescent. The solution cannot be concentrated by boiling, or the salt is precipitated as a basic salt.

Mercurous sulphate is formed by the action of excess of mercury on hot sulphuric acid.

It is also formed by adding sulphuric acid to a solution of mercurous nitrate.

$$\left. \begin{matrix} \text{mercurous} \\ \text{nitrate} \end{matrix} \right. + \left. \begin{matrix} \text{sulphuric} \\ \text{acid} \end{matrix} \right\} \text{form} \left\{ \begin{matrix} \text{mercurous} \\ \text{sulphate} \end{matrix} \right. + \left. \begin{matrix} \text{nitric} \\ \text{acid.} \end{matrix} \right.$$
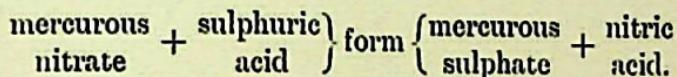
The mercurous sulphate forms a white crystalline precipitate which is slightly soluble in water.

Mercurous Chloride (calomel).—Mercurous chloride is manufactured by heating together mercuric chloride and mercury.

It may be prepared by the addition of hydrochloric acid to a solution of mercurous nitrate.

$$\left. \begin{matrix} \text{mercurous} \\ \text{nitrate} \end{matrix} \right. + \left. \begin{matrix} \text{hydrochloric} \\ \text{acid} \end{matrix} \right\} \text{form} \left\{ \begin{matrix} \text{mercurous} \\ \text{chloride} \end{matrix} \right. + \left. \begin{matrix} \text{nitric} \\ \text{acid.} \end{matrix} \right.$$
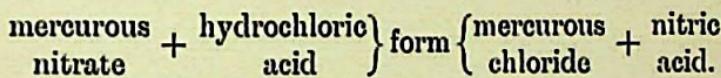
It may also be prepared by reducing mercuric chloride by means of phosphorous acid.

Mercurous chloride is an amorphous white powder, which is insoluble in water and in acids. Nitric acid oxidizes the salt into mercuric chloride. When heated alone, mercurous chloride sublimes; heated with carbon, it is reduced to metallic mercury.

Mercuric Chloride (corrosive sublimate).—This salt is usually prepared by heating together mercuric sulphate with about half its weight of common salt.

$$\left. \begin{matrix} \text{mercuric} \\ \text{sulphate} \end{matrix} \right. + \left. \begin{matrix} \text{sodium} \\ \text{chloride} \end{matrix} \right\} \text{form} \left\{ \begin{matrix} \text{mercuric} \\ \text{chloride} \end{matrix} \right. + \left. \begin{matrix} \text{sodium} \\ \text{sulphate.} \end{matrix} \right.$$
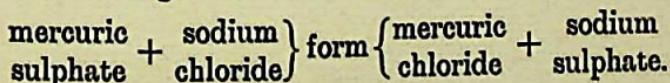
On heating the mixture the mercuric chloride sublimes (see p. 23), leaving the sodium sulphate behind. Mercuric chloride

is soluble in water, and crystallizes from hot solutions in the form of needles.

The solution is a powerful antiseptic. Like the other salts of mercury, mercuric chloride is poisonous, but is used in medicine in small quantities.

Mercuric sulphide is found native.

It can be prepared by grinding mercury and sulphur together in a mortar. It is precipitated as a black powder by passing sulphuretted hydrogen through a solution of a mercuric salt.

$$\left.\begin{matrix} \text{mercuric} \\ \text{chloride} \end{matrix}\right\} + \begin{matrix} \text{hydrogen} \\ \text{sulphide} \end{matrix} \Big\} \text{ form } \left\{ \begin{matrix} \text{mercuric} \\ \text{sulphide} \end{matrix} + \begin{matrix} \text{hydrochloric} \\ \text{acid.} \end{matrix}\right.$$
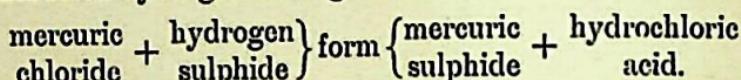
Mercuric sulphide can be obtained as a bright-red powder by subliming the black form. This red mercuric sulphide is used as a pigment under the name of "vermilion".

QUESTIONS ON CHAPTER XXV

1. Describe the preparation of mercury from mercuric chloride.

2. What do you understand by the terminations "-ous" and "-ic" as applied to metallic salts? Explain generally how you would convert a salt of the former into a salt of the latter type. Illustrate your answer by an example. (C. L.)

3. What compounds does mercury form with chlorine? How would you (a) prepare a specimen of one of them? (b) convert it into the other?

4. Describe the preparation of (a) zinc carbonate, (b) zinc sulphate, from metallic zinc.

5. Give an outline of the metallurgy of either mercury or zinc. State the chief characters and uses of the metal you select. (C. L.)

CHAPTER XXVI

COPPER AND SILVER

Copper.—Occurrence.—Copper is usually found in combination in its various ores, although the metal itself is mined in Canada round Lake Superior. The chief copper ores are those which contain cuprous oxide, cuprous sulphide (copper glance), cuprous and iron sulphides (copper pyrites), and basic copper carbonate. The occurrence of metallic copper is indicative of the fact that copper has little affinity for oxygen.

Copper has been known from very early times. The alchemists knew that
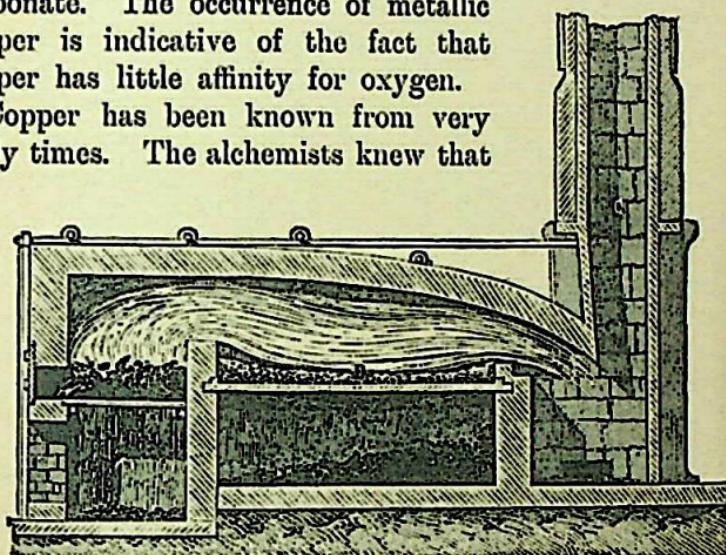
Fig. 113.—Reverberatory Furnace

D, Ore on bed of furnace. c, Chimney to carry off the waste gases.

it could be obtained from blue vitriol (copper sulphate) by the addition of iron to a solution of that salt (see p. 118). They explained the production of copper in this way by saying that the iron was changed to copper. Probably this was one of the reasons for their belief in the transmutation of metals.

Extraction.—The production of copper from its ores consists of a series of somewhat complicated operations, especially when the ore contains sulphur.

(i) Such ores are usually roasted in a reverberatory furnace (fig. 113) in such a way as to oxidize most of the iron to iron

oxide, some of the sulphur to sulphur dioxide, and to leave the copper as cuprous sulphide.

(ii) The roasted mass may then contain copper sulphide, iron oxide, silica, copper oxide, and some iron sulphide. It is then heated to a higher temperature to cause the iron oxide and silica to combine and form iron silicate. The iron silicate with other impurities fuse and form what is called the slag.

$$\text{iron oxide} + \text{silica} = \text{iron silicate}.$$

(iii) Operations (i) and (ii) are repeated, adding silica if necessary, until most of the iron has entered the slag.

(iv) The mass is then heated gently, in air, in order to convert some of the copper sulphide into copper oxide.

$$\left.\begin{array}{c}\text{copper} \\ \text{sulphide}\end{array}\right\} + \text{oxygen} \right\} \text{form} \left\{\begin{array}{c}\text{copper} \\ \text{oxide}\end{array} + \begin{array}{c}\text{sulphur} \\ \text{dioxide}.\end{array}\right.$$
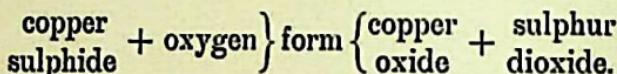
(v) The temperature is again raised, and the copper sulphide and copper oxide mutually decompose one another.

$$\left.\begin{array}{c}\text{copper} \\ \text{sulphide}\end{array} + \begin{array}{c}\text{copper} \\ \text{oxide}\end{array}\right\} \text{form} \left\{\text{copper} + \begin{array}{c}\text{sulphur} \\ \text{dioxide}.\end{array}\right.$$
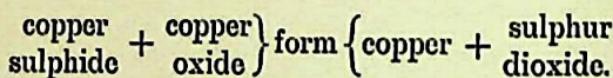
The large block of the impure copper so obtained is then

Fig. 114.—Refining Copper by Electrolysis

used as the anode in a bath of copper sulphate (fig. 114), through which an electric current is passed. The cathode is a thin sheet of copper. The current causes the impure copper to go into solution as copper sulphate, and at the same time liberates *pure* copper, which is deposited upon the cathode.

The last process—the refining of the copper—has a double advantage.

(i) It gives a very pure metal (99·8 per cent copper), which is a necessity if the copper is to be used for electrical work.

(ii) It enables the small quantities of silver and gold which are often present with the copper to be recovered. The silver and gold compounds collect as a slime at the bottom of the tank, and from them silver and gold are extracted.

Properties.—Copper is a salmon-pink coloured metal which quickly turns red when exposed to the air. It has a high melting-point (1080° C.) and a density of about 8·95. It is very malleable and ductile, but if heated and slowly cooled it gradually becomes brittle. Copper is one of the best conductors of heat and electricity and is therefore largely used for these purposes.

Dry air is without action upon copper. Under ordinary atmospheric conditions however—that is, in the presence of oxygen, carbon dioxide, and moisture—copper becomes coated with a green basic copper carbonate (verdigris).

Copper is not attacked by cold hydrochloric acid. Even boiling concentrated hydrochloric acid only attacks the metal slowly, forming an insoluble white powder, cuprous chloride.

Similarly, cold sulphuric acid, in the absence of air, has no effect upon copper. Hot concentrated sulphuric acid, however, readily dissolves the metal, with the formation of copper sulphate (see Experiment 49).

Nitric acid, even the cold dilute acid, dissolves copper readily, forming copper nitrate.

Copper forms a series of salts called cuprous salts and a series called cupric salts. The distinction between the two series is similar to that drawn between mercurous and mercuric salts (see p. 273).

Silver.—Occurrence.—Like copper, silver has little affinity for oxygen, and is therefore sometimes found in the metallic state. In its ores, silver occurs as silver sulphide (silver glance), as silver chloride, and in small quantities in lead ores (see p. 285). The silver obtained in the purification of lead amounts to about one-third of the world's supply.

Extraction.—There are many processes in use for the

extraction of silver from its ores. The most important method is by means of potassium cyanide. The ore is crushed and then added to a bath of potassium cyanide. The silver contained in the ore dissolves in the potassium cyanide, forming a double cyanide of silver and potassium. Just as iron will displace copper from copper sulphate, so will zinc displace silver from silver cyanide. Hence on adding zinc to the solution of silver and potassium cyanides, a double cyanide of zinc and potassium is formed and silver is precipitated.

Properties.—

	Copper.	Silver.
Melting-point ...	1080° C.	960° C.
Density... ...	8·95	10·5
Colour	Red.	Lustrous white.
Malleability ...	Malleable, unless heated and slowly cooled, when it becomes brittle.	Malleable. Can be hammered into sheets $\frac{1}{30000}$ cm. thick.
Ductility ...	Very ductile.	Very ductile.
Conductivity ...	Very high.	Higher than that of copper.

Silver is unaffected by air unless the air contains sulphuretted hydrogen. If sulphuretted hydrogen be present, silver readily blackens.

$$\text{silver} + \left.\begin{matrix}\text{hydrogen}\\\text{sulphide}\end{matrix}\right\} \text{form} \left\{\begin{matrix}\text{silver}\\\text{sulphide}\end{matrix}\right. + \text{hydrogen}.$$
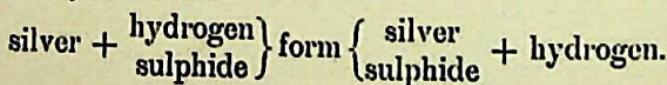
Hydrochloric acid is without effect upon silver, as also is cold sulphuric acid. Hot concentrated sulphuric acid dissolves the metal, forming silver sulphate. Nitric acid, either hot or cold, will also dissolve silver, forming silver nitrate. Silver is chiefly used for coinage and for ornaments. English "sterling silver" contains $92\frac{1}{2}$ per cent silver and $7\frac{1}{2}$ per cent copper.

Oxides of Copper.—(i) *Cupric Oxide.*—When copper is heated

in air or oxygen it oxidizes to a black hygroscopic substance called cupric oxide. The same oxide is readily obtained by heating copper hydroxide,[1] copper carbonate, or copper nitrate.

$$\left. \begin{matrix} \text{copper} \\ \text{carbonate} \end{matrix} \right\} \text{forms} \left\{ \begin{matrix} \text{copper} \\ \text{oxide} \end{matrix} \right. + \text{carbon dioxide.}$$
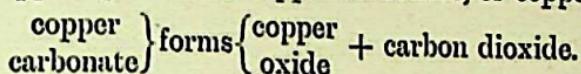
On heating cupric oxide to high temperatures it is gradually reduced to cuprous oxide.

Cupric oxide is readily reduced to copper by heating it with carbon or in a stream of hydrogen or carbon monoxide (see p. 70).

(ii) *Cuprous Oxide.*—If sodium potassium tartrate be added to a solution of copper sulphate, on adding potassium hydroxide to the solution and warming, a red precipitate of cuprous oxide is formed Glucose may be used instead of sodium potassium tartrate as the reducing agent in this reaction if desired.

Both these oxides of copper are weak bases. In combination with acids, cupric oxide gives rise to cupric salts and cuprous oxide forms cuprous salts.

Silver Oxide.—Silver oxide is formed on the addition of potassium hydroxide to a solution of silver nitrate. The brown powder which is precipitated, if dried at 100° C. yields silver oxide.

The union between the silver and oxygen is very weak however, so that on heating the silver oxide to a higher temperature (250° C.) metallic silver and oxygen are obtained.

Copper Hydroxide.—When potassium hydroxide is added to a solution of a soluble copper salt a greenish precipitate of copper hydroxide is formed.

$$\left. \begin{matrix} \text{copper} \\ \text{sulphate} \end{matrix} \right. + \left. \begin{matrix} \text{potassium} \\ \text{hydroxide} \end{matrix} \right\} \text{form} \left\{ \begin{matrix} \text{potassium} \\ \text{sulphate} \end{matrix} \right. + \begin{matrix} \text{copper} \\ \text{hydroxide.} \end{matrix}$$
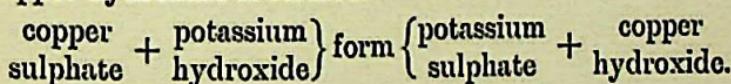
If the solution containing the copper hydroxide be boiled, the copper hydroxide loses the elements of water and becomes black copper oxide.

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[1] The adjective "copper" used in such terms throughout the book means "cupric".

Ammonium hydroxide gives a similar precipitate of copper hydroxide, but the precipitate dissolves in excess of ammonium hydroxide, forming a blue solution. The formation of this blue solution is a characteristic test for copper salts in analysis.

Copper Chlorides.—(i) *Cupric chloride* is a brown deliquescent powder. The hydrated salt is of a yellowish-green colour.

It may be formed by boiling cupric oxide with hydrochloric acid. A yellow solution containing cupric chloride is obtained.

$$\left. \begin{array}{c} \text{cupric} \\ \text{oxide} \end{array} + \begin{array}{c} \text{hydrochloric} \\ \text{acid} \end{array} \right\} \text{form} \left\{ \begin{array}{c} \text{cupric} \\ \text{chloride} \end{array} + \text{water.} \right.$$
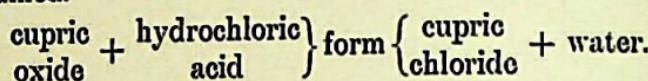
Green crystals of cupric chloride are deposited from the solution on evaporation. Cupric chloride is formed when copper is heated in excess of chlorine. With a limited supply of chlorine, cuprous chloride is formed.

(ii) *Cuprous Chloride.*—Cuprous chloride is a white powder generally obtained by reducing cupric chloride by zinc, copper, stannous chloride, or sulphurous acid.

Experiment 143.—Dissolve a little copper oxide in concentrated hydrochloric acid. Boil the solution with copper turnings for some time. Then pour the solution into a beaker of cold water, and a white precipitate of cuprous chloride will be formed. Filter off the cuprous chloride after removing any remaining copper. Wash the precipitate with water and dry it in a steam oven. Examine the solubility of the cuprous chloride so obtained in (i) ammonia, (ii) concentrated hydrochloric acid.

Silver Chloride.—This salt is obtained as a curdy, white precipitate on adding hydrochloric acid or a soluble chloride to a solution of silver nitrate.

$$\left. \begin{array}{c} \text{sodium} \\ \text{chloride} \end{array} + \begin{array}{c} \text{silver} \\ \text{nitrate} \end{array} \right\} \text{form} \left\{ \begin{array}{c} \text{sodium} \\ \text{nitrate} \end{array} + \begin{array}{c} \text{silver} \\ \text{chloride.} \end{array} \right.$$
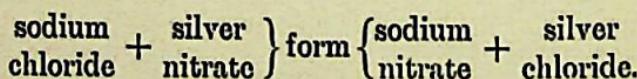
On exposure to sunlight, silver chloride turns violet, then brown, and finally black. It is almost insoluble in water and

in most acids, but dissolves readily in ammonium hydroxide, sodium sulphite, or sodium thiosulphate.

The action of light upon silver chloride is made use of in photography. Silver bromide is acted upon by light in a similar manner, and is used in photography in preference to silver chloride.

Cupric Sulphate (copper sulphate).—Copper sulphate may be prepared by dissolving copper oxide in sulphuric acid.

$$\text{copper oxide} + \text{sulphuric acid} \Big\} \text{form} \Big\{ \text{copper sulphate} + \text{water.}$$
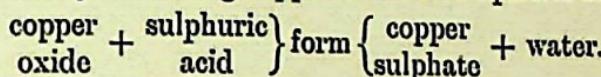
It is prepared commercially by roasting the ore called copper pyrites (see p. 277) in air. The cuprous sulphide is thus oxidized to cupric sulphate and the iron sulphide in the ore is replaced by iron oxide. On adding water to the roasted mass the copper sulphate dissolves, leaving the iron oxide behind. Copper sulphate prepared in this way contains iron sulphate as an impurity.

When pure copper sulphate is required, the copper is precipitated from the impure solution by means of scrap-iron (see p. 277). The precipitated copper is dissolved in sulphuric acid, forming copper sulphate solution, from which the pure salt crystallizes out in blue crystals. On heating the blue crystals of copper sulphate to 250° C. they part with their water of crystallization and form a white hygroscopic powder. This powder is used in the laboratory as a desiccating (drying) agent and also as a test for water (see Experiment 18).

Copper sulphate has many uses. It is employed in some electric batteries; in copper plating, that is, depositing a covering of copper upon articles by means of a current of electricity; and in dyeing.

Silver sulphate is formed when silver oxide or silver carbonate is dissolved in sulphuric acid:

$$\text{silver carbonate} + \text{sulphuric acid} \Big\} \text{form} \Big\{ \text{silver sulphate} + \text{water} + \text{carbon dioxide.}$$
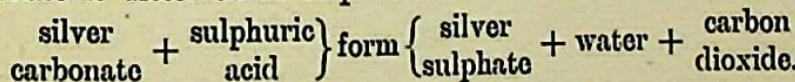
Cupric Nitrate.—This salt is formed when copper, copper oxide, or copper carbonate is dissolved in nitric acid. It

crystallizes in deliquescent blue crystals containing water of crystallization. The anhydrous salt has not been prepared, owing to the fact that, on heating, the crystals decompose, forming basic copper nitrate.

Silver nitrate is the most important soluble salt of silver. It may be obtained by the typical methods of preparing salts (see p. 305). It is usually obtained by dissolving silver in nitric acid.

$$\text{silver} + \left.\begin{matrix}\text{nitric}\\\text{acid}\end{matrix}\right\} \text{form} \left\{\begin{matrix}\text{silver}\\\text{nitrate}\end{matrix} + \begin{matrix}\text{oxides of}\\\text{nitrogen.}\end{matrix}\right.$$
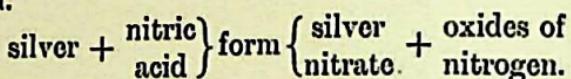
Silver nitrate is readily soluble in water, from which it crystallizes in anhydrous plates. In contact with organic matter—for example, the skin—it turns black. This property is taken advantage of in the preparation of ink for marking linen, and in the use of sticks of fused silver nitrate in medicine as a cauterizing (burning) agent.

QUESTIONS ON CHAPTER XXVI

1. Describe the preparation of approximately pure specimens of copper sulphate and copper nitrate from copper oxide, and of copper oxide from copper sulphate. State the chemical actions which occur in the making of these preparations. (C. L.)

2. Describe in detail the methods you would adopt to obtain (a) copper oxide, (b) copper, from a solution of copper sulphate. (C. L.)

3. How would you prepare specimens of (a) copper oxide, (b) copper nitrate, from metallic copper?

CHAPTER XXVII

LEAD

Occurrence.— Lead ores are found widely distributed over the earth. The chief ore is lead sulphide (galena), which is mined in the United Kingdom, Germany, Spain, Belgium, America, and many other countries.

Metallic lead has been used from very early times, probably owing to the ease with which it is reduced from its ores.

Extraction.—Ores which are rich in lead are roasted in a reverberatory furnace (fig. 113) with the doors open and the temperature raised to a dull red heat. Under these conditions the lead sulphide is oxidized partly to lead oxide and partly to lead sulphate.

(i) $\left.\begin{array}{c}\text{lead}\\\text{sulphide}\end{array}\right.$ + oxygen $\Big\}$ form $\left\{\begin{array}{l}\text{lead}\\\text{oxide}\end{array}\right.$ + $\begin{array}{l}\text{sulphur}\\\text{dioxide.}\end{array}$

(ii) $\left.\begin{array}{c}\text{lead}\\\text{sulphide}\end{array}\right.$ + oxygen $\Big\}$ form $\left\{\begin{array}{l}\text{lead}\\\text{sulphate.}\end{array}\right.$
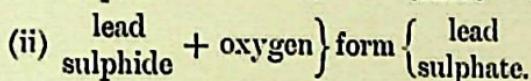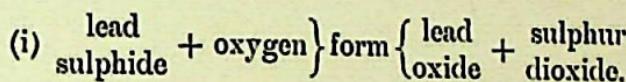
The doors of the furnace are then closed, and the temperature raised. The remaining lead sulphide then reacts with the lead oxide and lead sulphate to form lead and sulphur dioxide.

(iii) $\left.\begin{array}{c}\text{lead}\\\text{oxide}\end{array}\right.$ + $\left.\begin{array}{c}\text{lead}\\\text{sulphide}\end{array}\right\}$ form $\left\{\text{lead} + \begin{array}{l}\text{sulphur}\\\text{dioxide.}\end{array}\right.$

(iv) $\left.\begin{array}{c}\text{lead}\\\text{sulphate}\end{array}\right.$ + $\left.\begin{array}{c}\text{lead}\\\text{sulphide}\end{array}\right\}$ form $\left\{\text{lead} + \begin{array}{l}\text{sulphur}\\\text{dioxide.}\end{array}\right.$
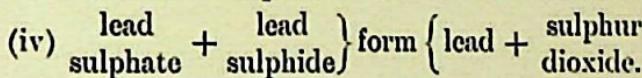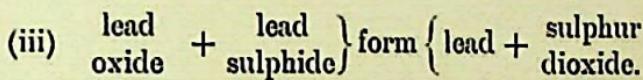
The molten lead runs down and collects in the depression in the hearth. The slag which collects, due to the earthy matters in the ore, contains about 10 per cent of the yield of lead. Lead so obtained contains many impurities; for example, antimony and silver. It is desirable to remove the antimony, since the presence of this metal makes the lead brittle. To bring about this removal the crude lead is heated in a reverberatory furnace, and the antimony and other impurities, which oxidize more readily than lead, form a scum on the surface of the molten metal. This scum is removed.

It is desirable to remove the silver because of its value. The method adopted depends upon this fact: when zinc is added to molten lead containing silver the zinc and silver unite to form a compound having a higher melting-point and a lower density than lead.

Zinc is therefore added to the molten lead which contains silver. On cooling, the compound of zinc and silver just men-

tioned floats on the top of the lead and solidifies into a crust while the lead is still molten. This crust is removed by means of a perforated ladle and heated on a sloping hearth. The lead melts, and most of it flows away, leaving the solid compound of silver and zinc on the hearth.

The zinc is separated from the silver and remaining lead by distilling the silver and zinc compound. The zinc is volatile and passes over into the receiver, leaving the silver in the still along with the lead which was not removed on the sloping hearth. This mixture is rich enough in silver to permit of a separation of the two metals by the following process, called cupellation.

Cupellation.—The alloy of lead and silver is heated in a furnace having a hearth lined with bone-ash. A current of air is blown over the surface of the heated mixture. The lead readily oxidizes to lead oxide (litharge), which floats on the molten silver. The litharge is partly removed and partly sinks into the bone-ash. When the whole of the lead has thus been oxidized and removed, the bright molten silver appears. The heating is then stopped, and the silver is thus obtained.

Properties of Lead.—

Melting-point ...	326° C.
Boiling-point ...	1536° C.
Density	11·3.
Malleability ...	Very malleable but not very ductile.
Hardness ...	Soft, can be cut with a knife; crystalline.
Colour	Bluish grey. Bright when freshly cut, but rapidly oxidizes on the surface.

Hydrochloric acid acts very slowly upon lead, because the metal becomes coated with lead chloride, which protects the lead underneath from the action of the acid.

Sulphuric acid, unless hot and concentrated, is practically

without action upon lead. Hence lead is used to line the chambers in the manufacture of sulphuric acid.

Nitric acid rapidly dissolves lead, forming lead nitrate (see p. 83).

$$\left.\text{lead} + \begin{array}{c}\text{nitric}\\\text{acid}\end{array}\right\} \text{form} \left\{\begin{array}{c}\text{lead}\\\text{nitrate}\end{array} + \begin{array}{c}\text{oxides of}\\\text{nitrogen.}\end{array}\right.$$
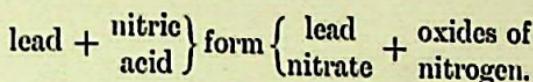
Lead is also somewhat soluble in distilled water containing oxygen. The presence of nitrates or calcium bicarbonate in the water renders the lead more soluble. This is probably brought about by the action of the dissolved oxygen in the water oxidizing the surface of the lead and forming lead oxide. The lead oxide combines with water to form lead hydroxide, which in turn combines with the carbon dioxide present to form basic lead carbonate. The further action of carbon dioxide upon this lead carbonate forms a soluble acid carbonate of lead (lead bicarbonate).

With calcium bicarbonate lead hydroxide forms lead bicarbonate (soluble).

With nitrates lead hydroxide forms lead nitrate (soluble).

In each of these cases much more lead goes into solution than would be the case if the lead hydroxide only were formed.

The presence of a sulphate in the water makes the lead much less soluble. This is due to the fact that the lead oxide or hydroxide and the sulphate react, forming lead sulphate (insoluble). The result is that the lead becomes coated with a layer of lead sulphate, which protects the metal from further action.

The importance of these observations will be realized when it is remembered that water for domestic purposes is supplied through lead pipes and that all lead salts are poisonous.

Lead is largely used for cisterns, sinks, roofing, and pipes. It also forms several useful alloys with other metals; for example, "solder" is an alloy of lead and tin, type-metal is an alloy of lead and antimony.

Lead Oxides.—(i) *Litharge.*—When lead is heated to a high temperature in air it combines with oxygen and forms reddish-

brown or yellow flakes. This compound is called *litharge or lead monoxide*.

A large quantity of litharge is obtained in the cupellation of lead and silver (see p. 286).

(ii) *Red Lead.*—When yellow lead monoxide is heated to a moderately high temperature in air or oxygen it is further oxidized, and forms a red powder called "red lead" or "minium". On further heating, red lead darkens in colour and *gives off* oxygen, changing at the same time into lead monoxide again. Thus red lead is a higher oxide (one containing a greater percentage of oxygen) than litharge.

(iii) *Lead Peroxide.*—Lead forms a still higher oxide than red lead. When nitric acid is added to red lead, lead nitrate is formed and dissolves, and a brown powder is precipitated. This brown powder is called lead peroxide.

When litharge is acted upon by nitric acid, lead nitrate is formed. Hence litharge is the ordinary basic oxide of lead.

$$\left.\begin{array}{c}\text{lead}\\\text{monoxide}\end{array} + \begin{array}{c}\text{nitric}\\\text{acid}\end{array}\right\} \text{form} \left\{\begin{array}{c}\text{lead}\\\text{nitrate}\end{array} + \text{water.}\right.$$
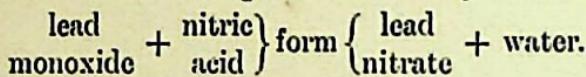
But when red lead is treated with nitric acid lead peroxide and lead nitrate are formed. This seems to indicate that red lead contains lead monoxide and lead peroxide, and that the lead monoxide reacts with the nitric acid, forming lead nitrate, and the lead peroxide remains.

$$\left.\begin{array}{c}\text{red}\\\text{lead}\end{array} + \begin{array}{c}\text{nitric}\\\text{acid}\end{array}\right\} \text{form} \left\{\begin{array}{c}\text{lead}\\\text{nitrate}\end{array} + \text{water} + \begin{array}{c}\text{lead}\\\text{peroxide.}\end{array}\right.$$
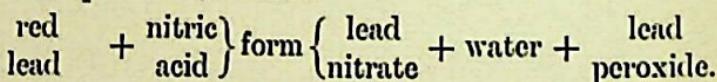
Like most peroxides, lead peroxide oxidizes hydrochloric acid into chlorine, and with sulphuric acid evolves oxygen.

$$(i) \begin{array}{c}\text{lead}\\\text{peroxide}\end{array} + \left.\begin{array}{c}\text{hydrochloric}\\\text{acid}\end{array}\right\} \text{form} \left\{\begin{array}{c}\text{lead}\\\text{chloride}\end{array} + \text{water} + \text{chlorine.}\right.$$

$$(ii) \begin{array}{c}\text{lead}\\\text{peroxide}\end{array} + \left.\begin{array}{c}\text{sulphuric}\\\text{acid}\end{array}\right\} \text{form} \left\{\begin{array}{c}\text{lead}\\\text{sulphate}\end{array} + \text{water} + \text{oxygen.}\right.$$
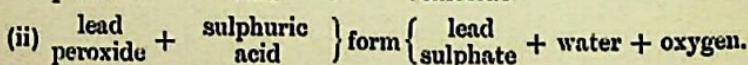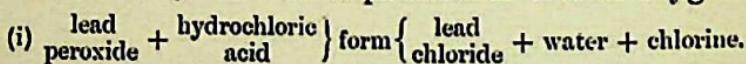
Like red lead, lead peroxide on heating strongly, evolves oxygen and changes to lead monoxide.

Lead peroxide is usually obtained by oxidizing a soluble lead salt by means of chlorine (see Experiment 144).

Uses.—Litharge is used in the glazing of pottery, and in the manufacture of flint glass, oils, and varnishes. Red lead is used as a colouring-matter in paint and in the manufacture of matches. The oxygen from the red lead supports the combustion of the materials on the head of the match.

Experiment 144.—To prepare lead peroxide.

Make a solution of lead nitrate in water. Add to it a solution of bleaching-powder (see p. 132). Warm the mixture, and notice the brown precipitate of lead peroxide which forms. Filter and wash the precipitate, and dry it in the steam oven.

Lead Hydroxide.—Litharge is slightly soluble in water, and the solution becomes weakly alkaline, due to the formation of lead hydroxide.

Like most of the insoluble or slightly soluble hydroxides, it is formed by adding caustic soda to a solution of a salt of the metal.

$$\left.\begin{matrix} \text{lead} \\ \text{nitrate} \end{matrix}\right\} + \left.\begin{matrix} \text{sodium} \\ \text{hydroxide} \end{matrix}\right\} \text{form} \left\{\begin{matrix} \text{lead} \\ \text{hydroxide} \end{matrix}\right. + \begin{matrix} \text{sodium} \\ \text{nitrate.} \end{matrix}$$
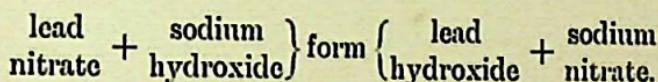
With a moderate quantity of caustic soda the lead hydroxide forms as a white precipitate. With excess of caustic soda the precipitate re-dissolves, forming sodium plumbite.

This means that with the strong base—caustic soda—lead oxide behaves like an acid oxide, whereas in its other reactions (see below) lead oxide acts as a basic oxide (see p. 248).

Lead oxide and lead hydroxide neutralize acids and form lead salts, e.g.:

$$\left.\begin{matrix} \text{lead} \\ \text{oxide} \end{matrix}\right\} + \left.\begin{matrix} \text{hydrochloric} \\ \text{acid} \end{matrix}\right\} \text{form} \left\{\begin{matrix} \text{lead} \\ \text{chloride} \end{matrix}\right. + \text{water.}$$
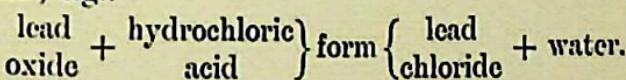
Lead Carbonate.—The usual method of forming the carbonates of the metals is by adding sodium carbonate to a solution of one of the salts of the metal. With lead salts, however, a basic carbonate[1] is precipitated.

$$\text{(i)} \quad \left.\begin{matrix} \text{sodium} \\ \text{carbonate} \end{matrix}\right\} + \left.\begin{matrix} \text{lead} \\ \text{nitrate} \end{matrix}\right\} \text{form} \left\{\begin{matrix} \text{sodium} \\ \text{nitrate} \end{matrix}\right. + \begin{matrix} \text{basic lead} \\ \text{carbonate.} \end{matrix}$$
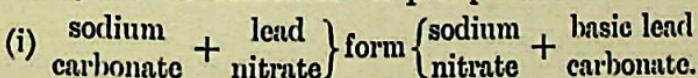
[1] There are several basic lead carbonates composed of the normal carbonate combined with different quantities of the base lead monoxide (see p. 92).

The normal carbonate has been formed by passing carbon dioxide into a dilute solution of "sugar of lead" (lead acetate).

(ii) $\left. \begin{array}{c} \text{lead} \\ \text{acetate} \end{array} + \text{water} + \begin{array}{c} \text{carbon} \\ \text{dioxide} \end{array} \right\}$ form $\left\{ \begin{array}{c} \text{lead} \\ \text{carbonate} \end{array} + \begin{array}{c} \text{acetic} \\ \text{acid.} \end{array} \right.$
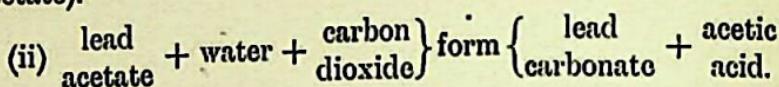
One of the basic carbonates of lead ("white lead") is very largely used as a pigment. It may be prepared by the action of carbon dioxide upon *basic* lead acetate.

Basic lead acetate may be prepared by boiling together lead acetate and lead oxide. On passing a current of carbon dioxide through the solution of basic lead acetate, a white precipitate of basic lead carbonate is formed.

(iii) $\left. \begin{array}{c} \text{lead} \\ \text{acetate} \end{array} + \begin{array}{c} \text{lead} \\ \text{oxide} \end{array} \right\}$ form $\left\{ \begin{array}{c} \text{basic lead} \\ \text{acetate.} \end{array} \right.$

(iv) $\left. \begin{array}{c} \text{basic lead} \\ \text{acetate} \end{array} + \begin{array}{c} \text{carbon} \\ \text{dioxide} \end{array} + \text{water} \right\}$ form $\left\{ \begin{array}{c} \text{basic lead} \\ \text{carbonate} \end{array} + \begin{array}{c} \text{acetic} \\ \text{acid.} \end{array} \right.$
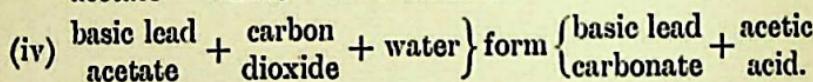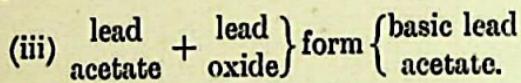
In the manufacture of white lead by what is known as the

Fig. 115.—Production of White Lead

A, Acetic acid.   L, Sheet lead.

"Dutch process" these reactions take place slowly and continuously.

Sheets of lead (L, fig. 115) are coiled up and placed on ledges in earthenware jars shaped somewhat as in the diagram. The bottom of the jar, A, is filled with acetic acid, and the jars are arranged on the floors of the room and covered with planks.

The planks are covered with a layer of bark tan or other decaying vegetation and another layer of jars is placed on top. In this way a stack of such jars is built up in the room. The heat from the decaying matter vaporizes the acetic acid, which, together with the oxygen, attacks the lead. This results in the formation of basic lead acetate (see (iii) above).

The decaying matters also give off quantities of carbon

dioxide, which react with the basic lead acetate to form basic lead carbonate (white lead). The acetic acid thus set free (see (iv) above) attacks another portion of the lead, so that the process is continuous.

Lead Sulphide.—When sulphuretted hydrogen is added to a solution of lead nitrate, a brownish-black precipitate of lead sulphide is formed.

$$\left.\begin{matrix}\text{lead} \\ \text{nitrate}\end{matrix} + \begin{matrix}\text{hydrogen} \\ \text{sulphide}\end{matrix}\right\} \text{form} \left\{\begin{matrix}\text{lead} \\ \text{sulphide}\end{matrix} + \begin{matrix}\text{nitric} \\ \text{acid.}\end{matrix}\right.$$
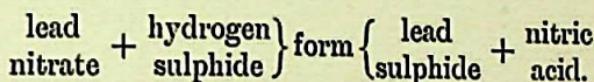
When damp lead sulphide is left exposed to the air it is gradually oxidized into lead sulphate.

$$\left.\begin{matrix}\text{lead} \\ \text{sulphide}\end{matrix} + \text{oxygen}\right\} \text{form} \left\{\begin{matrix}\text{lead} \\ \text{sulphate.}\end{matrix}\right.$$
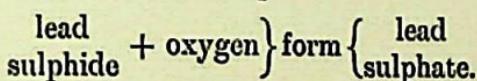
Lead sulphide may also be formed by heating together lead and sulphur. The elements combine and form lead sulphide.

$$\text{lead} + \text{sulphur} \quad \text{form} \quad \text{lead sulphide.}$$
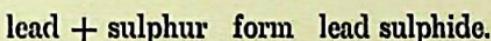
The blackening of white paint (basic lead carbonate) is due to the formation of lead sulphide by the action of the sulphuretted hydrogen in the air (see p. 165) upon the white lead.

Lead chloride may be formed by dissolving lead oxide in hydrochloric acid. It is more readily made by the addition of hydrochloric acid to a solution of lead nitrate. A white crystalline precipitate is formed. On warming the solution the lead chloride dissolves, being much more soluble in hot than in cold water. Crystals of lead chloride are re-formed on cooling.

$$\left.\begin{matrix}\text{lead} \\ \text{nitrate}\end{matrix} + \begin{matrix}\text{hydrochloric} \\ \text{acid}\end{matrix}\right\} \text{form} \left\{\begin{matrix}\text{lead} \\ \text{chloride}\end{matrix} + \begin{matrix}\text{nitric} \\ \text{acid.}\end{matrix}\right.$$
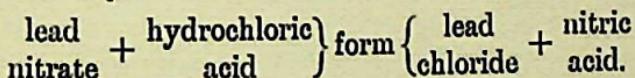
Lead Sulphate.—Lead sulphate is formed by adding sulphuric acid to a solution of lead nitrate or lead acetate. A heavy white precipitate of lead sulphate is formed which is almost insoluble in water but dissolves freely in hot concentrated hydrochloric acid.

$$\left.\begin{matrix}\text{lead} \\ \text{nitrate}\end{matrix} + \begin{matrix}\text{sulphuric} \\ \text{acid}\end{matrix}\right\} \text{form} \left\{\begin{matrix}\text{lead} \\ \text{sulphate}\end{matrix} + \begin{matrix}\text{nitric} \\ \text{acid.}\end{matrix}\right.$$

Lead Nitrate.—This salt may be prepared by the typical methods of preparing salts; that is, by dissolving the metal, its oxide, or its carbonate in the required acid. For example—

$$\left.\begin{array}{l}\text{lead}\\\text{carbonate}\end{array}+\begin{array}{l}\text{nitric}\\\text{acid}\end{array}\right\}\text{form}\left\{\begin{array}{l}\text{lead}\\\text{nitrate}\end{array}+\text{water}+\begin{array}{l}\text{carbon}\\\text{dioxide.}\end{array}\right.$$
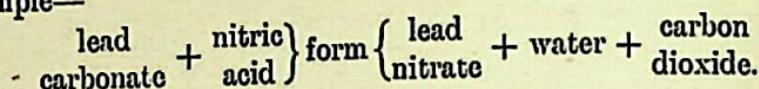
Lead nitrate, the chief soluble salt of lead, is a white crystalline solid which, on heating, is decomposed, forming litharge, oxygen, and nitrogen peroxide.

Experiment 145.—To prepare nitrogen peroxide. Place about 20 grm. of dry lead nitrate in a retort. Connect the retort to two or three U-tubes immersed in a freezing-mixture of ice and salt. Heat the retort and its contents and the nitrogen peroxide will collect as a liquid which sets to a white solid at − 9° C. The liquid boils at 22° C. and forms a dense red gas which has a suffocating odour and is very corrosive. The gas is very soluble in water, forming nitrous and nitric acids. It also dissolves in caustic soda, forming a mixture of sodium nitrite and sodium nitrate.

QUESTIONS ON CHAPTER XXVII

1. Describe the preparation of crystals of lead chloride from lead oxide.

2. How is "white lead" prepared commercially? Give an explanation of the reactions which occur.

3. Describe the preparation of lead peroxide from lead acetate.

4. Name a common ore of lead. Give an outline of the process whereby lead is obtained from the ore you mention, paying particular attention to the chemical changes which occur in the preparation. (C. L.)

5. Give an outline of the metallurgy of either lead or zinc. State the most important uses of the metal you select. (C. L.)

6. State what you know about the oxides of lead. How would you obtain lead from lead oxide and mercury from mercuric oxide? (C. L.)

CHAPTER XXVIII

IRON

Occurrence.—Iron is readily oxidized, and is therefore seldom found free in nature. The metal is, however, found uncombined in Greenland. The chief ores of iron are—

(i) Magnetite (magnetic oxide of iron), found in Sweden, Siberia, and North America.

(ii) Hæmatite (red oxide of iron), found in Sweden, Belgium, and round Lake Superior.

(iii) Clay ironstone (iron carbonate containing a quantity of clay).

Extraction.— The extraction of iron from its ores usually consists of two processes.

(i) *Calcining.*—The ore is first built into

Fig. 116.—Blast Furnace (diagrammatic)

piles with coal and calcined (burned). The object of the calcining is to get rid of any arsenic or sulphur present in the ore, since such substances would adversely affect the properties of the iron. This separation is brought about by adjusting the air supply so that the sulphur burns to sulphur dioxide, and the iron carbonate, for example, is decomposed into iron oxide and carbon dioxide. At the same time the

moisture is expelled from the ore by the heat and a porous mass remains.

(ii) *Smelting.*—The calcined ore is mixed with half its bulk of coke and about one-quarter of its bulk of limestone. This mixture is introduced into a blast-furnace (fig. 116) at A by lowering the cone C.

Near the bottom of the furnace are openings called tuyères (T), through which a blast of heated air is forced. [This air-blast is heated by passing it through a tower made hot by burning in it the gases which escape at G. These gases contain about 25 per cent of carbon monoxide (see p. 192).] The oxygen in the air-blast combines with the coke (carbon) to form carbon monoxide (see p. 188).

This carbon monoxide rising through the furnace meets the descending iron oxide in the upper part of the furnace, where the temperature is about 700° C. Here the carbon monoxide reduces the iron oxide to iron.

$$\left.\begin{matrix} \text{iron} \\ \text{oxide} \end{matrix}\right\} + \left.\begin{matrix} \text{carbon} \\ \text{monoxide} \end{matrix}\right\} \text{form} \left\{ \text{iron} + \begin{matrix} \text{carbon} \\ \text{dioxide.} \end{matrix} \right. \tag{i}$$
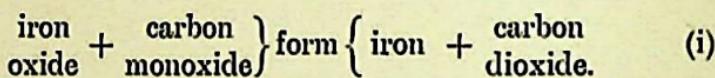
Lower down the furnace, where the temperature is higher, the reverse reaction takes place, and some of the iron is oxidized again.

$$\text{iron} + \left.\begin{matrix} \text{carbon} \\ \text{monoxide} \end{matrix}\right\} \text{form} \left\{ \begin{matrix} \text{iron} \\ \text{oxide} \end{matrix} + \text{carbon.} \right. \tag{ii}$$
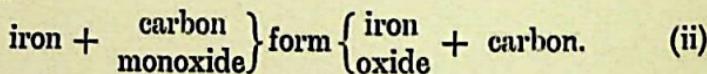
In this region the temperature is high enough to decompose the limestone. The carbon dioxide produced is reduced to carbon monoxide by the coke.

$$\left.\begin{matrix} \text{calcium} \\ \text{carbonate} \end{matrix}\right\} \text{forms} \left\{ \begin{matrix} \text{calcium} \\ \text{oxide} \end{matrix} + \begin{matrix} \text{carbon} \\ \text{dioxide.} \end{matrix} \right. \tag{iii}$$

$$\left.\begin{matrix} \text{carbon} \\ \text{dioxide} \end{matrix}\right\} + \text{carbon} \right\} \text{form} \left\{ \text{carbon monoxide.} \tag{iv}$$
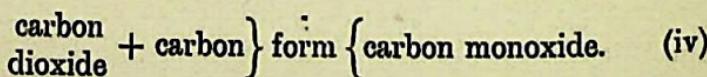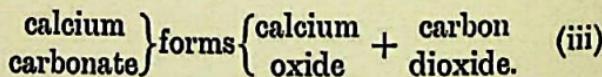
The temperature lower down the furnace is higher still (about 1000° C.). In this region, the ascending carbon monoxide is unstable owing to the high temperature. One volume

of carbon monoxide reduces another volume of carbon monoxide, being itself oxidized.

$$\left.\begin{array}{c}\text{carbon} \\ \text{monoxide}\end{array} + \begin{array}{c}\text{carbon} \\ \text{monoxide}\end{array}\right\} \text{form} \left\{\begin{array}{c}\text{carbon} \\ \text{dioxide}\end{array} + \text{carbon.}\right. \quad \text{(v)}$$
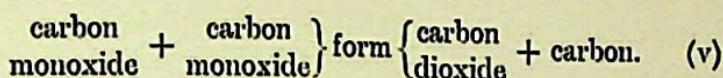
The carbon so produced reduces the iron oxide formed as in (ii) to iron.

$$\left.\begin{array}{c}\text{iron} \\ \text{oxide}\end{array} + \text{carbon}\right\} \text{form} \left\{\text{iron} + \begin{array}{c}\text{carbon} \\ \text{monoxide.}\end{array}\right. \quad \text{(vi)}$$
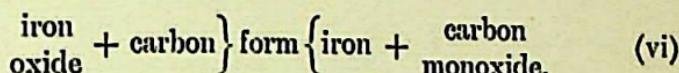
In this, the hottest region, the lime formed from the limestone (see (iii) above) and the aluminium oxide present in the clay of the ore combine with the silica, which is also present in the ore, to form silicates of calcium and aluminium (see p. 244).

$$\left.\begin{array}{l}\begin{array}{c}\text{calcium} \\ \text{oxide}\end{array} + \text{silica}\right\} \text{form} \left\{\text{calcium silicate.}\right. \\ \begin{array}{c}\text{aluminium} \\ \text{oxide}\end{array} + \text{silica}\right\} \text{form} \left\{\text{aluminium silicate.}\right. \end{array}\right\} \quad \text{(vii)}$$
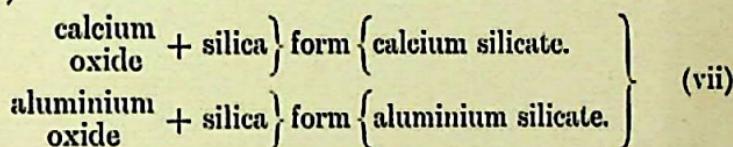
These silicates are liquid at the high temperature of the furnace and dissolve other impurities, forming what is called the "slag".

The iron at the temperature of the middle of the furnace is not molten, but exists in a pasty condition. Further down the furnace, near the base, the iron dissolves a quantity of carbon and becomes molten. The molten iron collects on the hearth of the furnace D, and the lighter slag floats on the molten iron. Openings are provided (i) at E for running off the molten slag, and (ii) at F for running off the molten iron. The iron is drawn off once every twelve hours, and runs into channels in a bed of sand. The bars of iron so obtained are called "pigs", and the iron is known as pig-iron or cast iron. In "grey" pig-iron most of the carbon is uncombined or free, whereas in "white" pig-iron practically the whole of the carbon is combined with the iron.

Wrought Iron.—Pig-iron contains, in addition to about 3 per cent of carbon, variable quantities of sulphur, phos-

phorus, and silicon. These impurities are dissolved out of the ore by the iron in its passage through the blast-furnace. The presence of these impurities makes the iron brittle, and for some purposes this is a disadvantage. The impurities are removed from the iron by heating pig-iron with iron oxide in a puddling furnace. By admitting a suitable quantity of air, and puddling or working the mixture, the impurities are oxidized and escape or form a slag. The metal is then hammered and rolled while still hot, and any slag present in the metal is squeezed out. The wrought iron so obtained is very pure iron, containing less than 1 per cent of impurities.

Steel.—In the preparation of wrought iron most of the carbon in the pig-iron is removed as well as the other impurities. In metal used for making tools and for other purposes the removal of almost the whole of the carbon is a disadvantage. Carbon is therefore introduced into the wrought iron.

In one process, bars of wrought iron are heated (not melted) with carbon in ovens or retorts. A small quantity of the carbon is gradually absorbed by the iron, and in a week or two the required quantity of carbon has been absorbed. The material is then called "steel".

"Cast steel" is made by melting wrought iron in graphite crucibles with the requisite quantity of carbon. Cast steel is a very expensive steel, and is mainly used in the manufacture of cutting tools which are required to be very hard.

Another process for converting wrought iron or even pig-iron into steel is called the Bessemer process, after its inventor. In this process the iron is melted and then introduced into a large iron vessel called a "converter" (fig. 117). The converter is lined with silica or lime or magnesium oxide. The material lining the converter combines with the impurities in the iron and forms a slag.

A blast of air is blown through the molten metal in A by way of the pipe D. After about a quarter of an hour the impurities in the iron, including the carbon, have been oxidized, and will either have escaped as gases (sulphur dioxide and

carbon monoxide) or will have combined with the lining to form a slag (calcium phosphate, calcium silicate, &c.).

The amount of carbon required to convert the iron into steel is then added, and the blast continued for a few minutes to facilitate mixing.
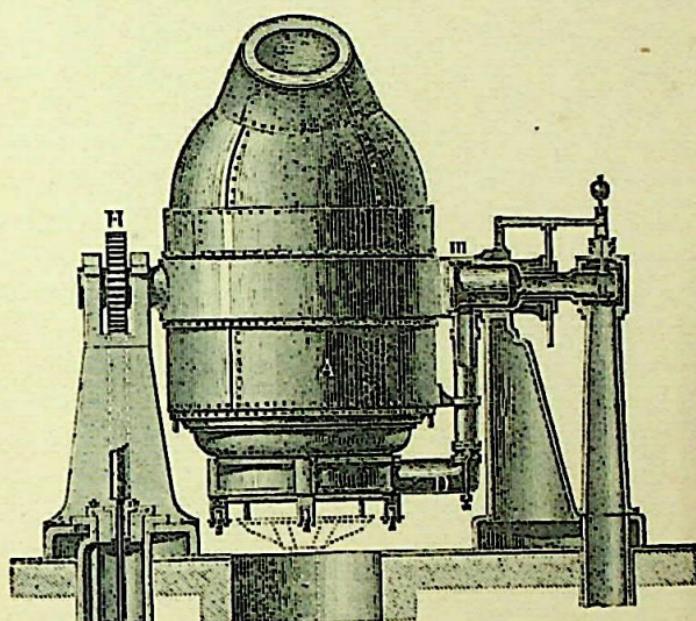
Fig. 117.—Bessemer Converter

A, Body of converter, which swings on the pivots at H and m. D, Tube for conveying air to molten metal.

Oxides of Iron.—Iron forms three oxides—(i) ferrous oxide, which forms ferrous salts; (ii) ferric oxide, which forms ferric salts; (iii) magnetic oxide of iron, which forms a mixture of ferrous and ferric salts on treatment with hydrochloric or sulphuric acid.

Ferrous oxide may be formed by reducing ferric oxide by means of hydrogen. The ferric oxide must not be heated above 300° C.

$$\left.\begin{matrix} \text{ferric} \\ \text{oxide} \end{matrix} + \text{hydrogen}\right\} \text{form} \left\{\begin{matrix} \text{ferrous} \\ \text{oxide} \end{matrix} + \text{water.}\right.$$
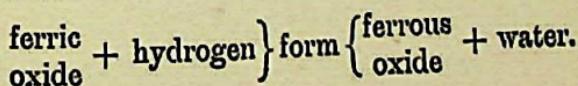
Further action of hydrogen reduces the ferrous oxide to metallic iron.

Ferrous oxide is a black substance which readily unites with the oxygen of the air to form ferric oxide.

Ferric oxide occurs naturally. It may be formed by heating ferrous sulphate strongly.

$$\left.\begin{array}{c}\text{ferrous}\\\text{sulphate}\end{array}\right\}\text{forms}\left\{\begin{array}{c}\text{ferric}\\\text{oxide}\end{array}+\begin{array}{c}\text{sulphur}\\\text{trioxide.}\end{array}\right.$$
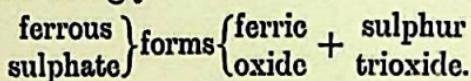
Ferric oxide is a red powder, and is used both as a pigment and for polishing purposes.

Magnetic oxide of iron occurs naturally. When iron is strongly heated in steam the iron is oxidized to magnetic oxide of iron (see p. 57). Because of its colour, this oxide is also known as black oxide of iron. Ferric oxide is often called red oxide of iron for purposes of distinction.

Hydroxides of Iron.—(i) *Ferrous hydroxide* is formed as an immediate white precipitate on adding caustic soda to a solution of a ferrous salt.

$$\left.\begin{array}{c}\text{ferrous}\\\text{sulphate}\end{array}+\begin{array}{c}\text{sodium}\\\text{hydroxide}\end{array}\right\}\text{form}\left\{\begin{array}{c}\text{ferrous}\\\text{hydroxide}\end{array}+\begin{array}{c}\text{sodium}\\\text{sulphate.}\end{array}\right.$$
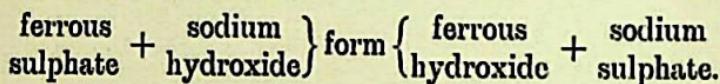
The precipitate, however, rapidly oxidizes in air, and turns green and then reddish brown, forming ferric hydroxide.

Ferrous hydroxide is soluble in acids with the formation of ferrous salts. These readily oxidize in air and form ferric salts.

(ii) *Ferric hydroxide* is obtained as a reddish-brown precipitate on the addition of caustic soda to a solution of a ferric salt.

$$\left.\begin{array}{c}\text{ferric}\\\text{sulphate}\end{array}+\begin{array}{c}\text{sodium}\\\text{hydroxide}\end{array}\right\}\text{form}\left\{\begin{array}{c}\text{ferric}\\\text{hydroxide}\end{array}+\begin{array}{c}\text{sodium}\\\text{sulphate.}\end{array}\right.$$
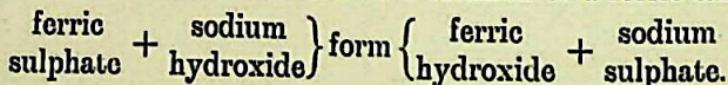
Ferric hydroxide readily dissolves in acids with the formation of ferric salts. Ordinary iron rust is mainly composed of ferric hydroxide.

Ferrous Sulphate (green vitriol).—When iron is dissolved in dilute sulphuric acid ferrous sulphate is formed.

$$\text{iron}+\left.\begin{array}{c}\text{sulphuric}\\\text{acid}\end{array}\right\}\text{form}\left\{\begin{array}{c}\text{ferrous}\\\text{sulphate}\end{array}+\text{hydrogen.}\right.$$
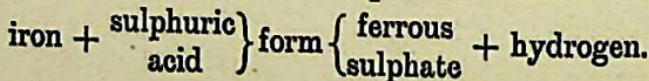
Unless precautions be taken to exclude air from the apparatus the ferrous sulphate oxidizes to ferric sulphate. One method of excluding the air during the operation is by means of a Bunsen valve. The flask containing the sulphuric acid and iron wire is fitted with a rubber stopper carrying a short piece of glass tubing (T, fig. 24). Affixed to T is a short length of rubber tubing R containing a slit lengthwise. The end of the rubber tubing is closed by means of a clip C. The hydrogen and steam produced when the contents of the flask are boiled can escape through the slit, but the air cannot enter the flask.

Ferrous sulphate can also be obtained by dissolving ferrous oxide in sulphuric acid. Ferrous sulphate is made commercially by exposing iron pyrites (iron sulphide) to the action of air and moisture. The iron sulphide is oxidized to iron sulphate.

When heated in closed vessels ferrous sulphate is decomposed. Sulphur trioxide and sulphuric acid distil over, forming a solution known as Nordhausen or fuming sulphuric acid. Red ferric oxide is left behind (see p. 298).

$$\left. \begin{matrix} \text{ferrous} \\ \text{sulphate} \end{matrix} \right\} \text{forms} \left\{ \begin{matrix} \text{sulphur} \\ \text{trioxide} \end{matrix} + \underbrace{\begin{matrix} \text{sulphuric} \\ \text{acid} \end{matrix}}_{} + \begin{matrix} \text{ferric} \\ \text{oxide.} \end{matrix} \right.$$

(Nordhausen sulphuric acid.)
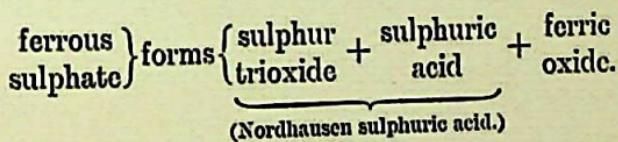
When solutions of ferrous sulphate and ammonium sulphate are mixed and the liquid concentrated, greenish-blue crystals of ferrous ammonium sulphate are formed. Salts like ferrous ammonium sulphate which are formed by the combination of two distinct salts are called *double salts*. (Contrast this with Experiment 129, p. 237.)

Ferrous sulphate forms double salts with the sulphates of sodium and potassium.

Ferrous ammonium sulphate is often used in the volumetric estimation of the amount of iron present in a given substance, because of all the ferrous salts it shows the least tendency to oxidize in air.

Ferric sulphate is formed when ferric oxide is dissolved in sulphuric acid.

$$\left.\begin{array}{c}\text{ferric}\\\text{oxide}\end{array} + \begin{array}{c}\text{sulphuric}\\\text{acid}\end{array}\right\} \text{form} \left\{\begin{array}{c}\text{ferric}\\\text{sulphate}\end{array} + \text{water.}\right.$$
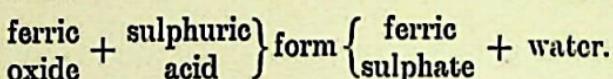
It may also be obtained by oxidizing a solution of ferrous sulphate. Such oxidation proceeds fairly quickly merely on exposure to the air. It is rapidly attained by boiling a mixture of sulphuric acid and ferrous sulphate solution with a few drops of nitric acid.

$$\left.\begin{array}{c}\text{sulphuric}\\\text{acid}\end{array} + \begin{array}{c}\text{ferrous}\\\text{sulphate}\end{array} + \begin{array}{c}\text{nitric}\\\text{acid}\end{array}\right\} \text{form} \left\{\begin{array}{c}\text{ferric}\\\text{sulphate}\end{array} + \begin{array}{c}\text{nitric}\\\text{oxide}\end{array} + \text{water.}\right.$$
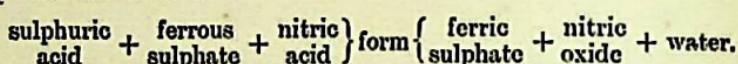
Ferric sulphate, like ferrous sulphate, forms double salts with the sulphates of sodium and potassium. For example, ferric ammonium sulphate crystals may be obtained by mixing solutions of ferric sulphate and ammonium sulphate, concentrating the solution, and allowing it to cool. The double salt thus obtained is called *iron alum*.

The term **alum** is applied to several double sulphates. All the alums contain—(i) sodium or potassium or ammonium sulphate, (ii) aluminium or chromium or ferric sulphate.

Alum or potash alum is the double sulphate of potassium and aluminium.

Ammonium alum is the double sulphate of ammonium and aluminium.

Chrome alum is the double sulphate of potassium and chromium.

The alums all crystallize in regular octahedra.

Ferrous Chloride.—When iron is dissolved in hydrochloric acid, and the solution concentrated, green crystals of ferrous chloride containing water of crystallization (the hydrated salt) are obtained.

$$\text{iron} + \left.\begin{array}{c}\text{hydrochloric}\\\text{acid}\end{array}\right\} \text{form} \left\{\begin{array}{c}\text{ferrous}\\\text{chloride}\end{array} + \text{hydrogen.}\right.$$
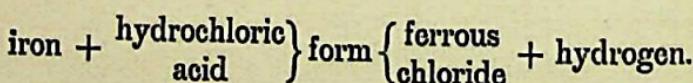
On heating ferrous chloride the salt decomposes. It is impossible, therefore, to form the anhydrous salt in this way.

Anhydrous ferrous chloride is obtained when iron is gently heated in a stream of dry hydrochloric acid gas.

Experiment 146.—To prepare anhydrous ferrous chloride.

The apparatus shown in fig. 118 may be used.
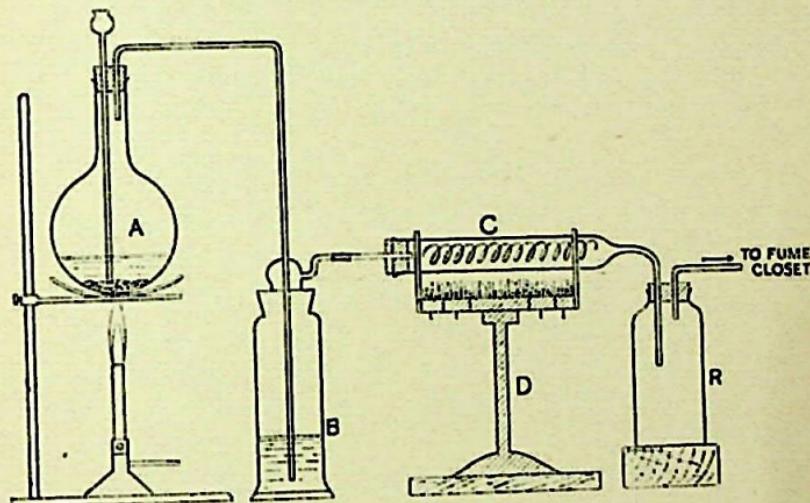
Fig. 118.—Preparation of Anhydrous Ferrous Chloride

The flask A contains common salt and sulphuric acid to generate hydrochloric acid.

The wash-bottle B contains concentrated sulphuric acid to dry the hydrochloric acid.

The combustion-tube C, which should be fairly wide, contains a coil of *fine* iron wire.

The receiver R is to collect the ferrous chloride formed. The outlet from R leads to the fume-closet, and serves to get rid of the unused gas.

Warm the mixture in A to displace the air, and fill the apparatus with hydrochloric acid gas. Then heat the tube C by means of the Ramsay burner D, and maintain the current of hydrochloric acid gas by warming A and adding concentrated sulphuric acid through the thistle-funnel if necessary. Examine the white crystals of ferrous chloride deposited in

R. Notice that they are deliquescent. Dissolve them in water and crystallize the salt from the solution.

Ferric chloride may be obtained by dissolving ferric oxide in hydrochloric acid.

$$\left.\begin{array}{c} \text{ferric} \\ \text{oxide} \end{array} + \begin{array}{c} \text{hydrochloric} \\ \text{acid} \end{array}\right\} \text{form} \left\{\begin{array}{c} \text{ferric} \\ \text{chloride} \end{array} + \text{water.}\right.$$
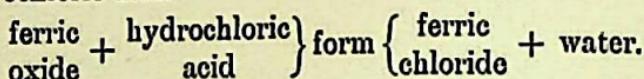
The salt so obtained is hydrated.

Anhydrous ferric chloride may be obtained by the action of chlorine on iron.

$$\text{iron} + \text{chlorine} \quad \text{form} \quad \text{ferric chloride.}$$
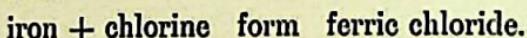
The apparatus shown in fig. 118 may be used, and the procedure is similar to that given in Experiment 146, except that the flask A contains manganese dioxide and hydrochloric acid.

Ferric chloride may also be obtained (in the hydrated form) by oxidizing a solution of ferrous chloride. Such oxidation is rapidly brought about by passing a stream of chlorine through the solution.

$$\left.\begin{array}{c} \text{ferrous} \\ \text{chloride} \end{array} + \text{chlorine}\right\} \text{form} \left\{\begin{array}{c} \text{ferric} \\ \text{chloride.} \end{array}\right.$$
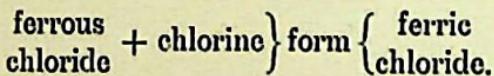
Ferrous sulphide has already been prepared (see p. 78) by the direct union of its elements. It may also be prepared by reducing ferrous sulphate by means of carbon.

$$\left.\begin{array}{c} \text{ferrous} \\ \text{sulphate} \end{array} + \text{carbon}\right\} \text{form} \left\{\begin{array}{c} \text{ferrous} \\ \text{sulphide} \end{array} + \begin{array}{c} \text{carbon} \\ \text{dioxide.} \end{array}\right.$$

When ammonium sulphide solution is added to a solution of a ferrous salt a black precipitate of ferrous sulphide is formed. The precipitate absorbs oxygen on exposure to the air and is converted into ferrous sulphate.

$$\left.\begin{array}{c} \text{ferrous} \\ \text{sulphate} \end{array} + \begin{array}{c} \text{ammonium} \\ \text{sulphide} \end{array}\right\} \text{form} \left\{\begin{array}{c} \text{ferrous} \\ \text{sulphide} \end{array} + \begin{array}{c} \text{ammonium} \\ \text{sulphate.} \end{array}\right.$$
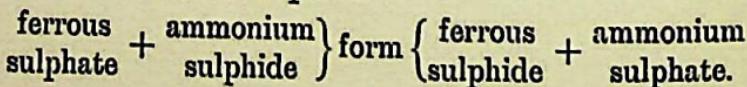
Ferrous sulphide is used in the laboratory in the preparation of sulphuretted hydrogen (see p. 163).

Iron pyrites is a higher sulphide of iron (see p. 288).

Iron Nitrates.—Ferrous nitrate is formed by the action of

cold dilute nitric acid upon iron. With the concentrated acid ferric nitrate is obtained.

Ferrous carbonate occurs naturally, and is an important iron ore. It may be prepared by adding ammonium carbonate solution to a ferrous salt.

$$\left.\begin{array}{l}\text{ferrous}\\\text{sulphate}\end{array}\right\} + \left.\begin{array}{l}\text{ammonium}\\\text{carbonate}\end{array}\right\} \text{form} \left\{\begin{array}{l}\text{ammonium}\\\text{sulphate}\end{array} + \begin{array}{l}\text{ferrous}\\\text{carbonate.}\end{array}\right.$$

QUESTIONS ON CHAPTER XXVIII

1. Describe the preparation of ferrous sulphate from ferric oxide, and of ferric oxide from ferrous sulphate, stating the chemical actions which occur, and indicating those which are reductions and those which are oxidations. (C. L.)

2. A blast-furnace is charged at the top with hæmatite, coke, and limestone, and melted slag and cast iron are drawn off at the bottom; describe the principal chemical changes which occur in the furnace. (C. L.)

3. How is iron converted into steel? What is meant by the tempering of steel, and what is the object of this process? (O. L.)

4. How would you proceed in order to obtain (i) ferric oxide from iron, (ii) iron from ferric oxide? (C. L.)

5. Describe in detail the methods you would use to obtain (*a*) iron from ferric oxide, (*b*) mercuric oxide from mercury. (C. L.)

CHAPTER XXIX

GENERAL METHODS OF PREPARING OXIDES, HYDROXIDES, AND SALTS OF METALS

Oxides.—(i) *Most metallic oxides may be prepared by calcining the metal in air.*

This method is most suitable for the preparation of the oxides of sodium, potassium, calcium, magnesium, and zinc, since these

metals burn in air. In the case of metals which do not ignite when heated in air, the surface of the metal is oxidized and the interior of the metal remains unchanged. This is what happens in the case of mercury, iron, lead, and copper. Hence, in the preparation of litharge (see p. 286) and mercuric oxide (see p. 44) by this method, the oxide is removed as it is formed, so as to allow free access of air to the unoxidized metal.

In the case of silver the oxide is decomposed into silver and oxygen at about 300° C. Lead, when calcined, may form either litharge or red lead. Which oxide is obtained depends upon the temperature to which the metal is heated (see p. 288).

(ii) *Metallic oxides may be prepared by heating the carbonate of the metal.*

This is true of all the carbonates except **sodium and potassium carbonates**. These carbonates do not decompose on being heated; the carbonates of the other metals do decompose, yielding carbon dioxide and the oxide of the metal, e.g.:

$$\left.\begin{matrix} \text{zinc} \\ \text{carbonate} \end{matrix}\right\} \text{forms} \left\{\begin{matrix} \text{zinc} \\ \text{oxide} \end{matrix} + \begin{matrix} \text{carbon} \\ \text{dioxide.} \end{matrix}\right.$$
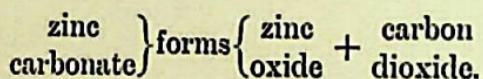
(iii) *Metallic oxides may be prepared by heating the nitrate of the metal.*

This method is most suitable for the preparation of the oxides of heavy metals—mercury, zinc, copper, and lead. It is not applicable in the case of potassium nitrate (which on being heated yields potassium nitrite and oxygen), nor in the case of silver nitrate, which yields metallic silver on being heated (see (i)).

(iv) *Metallic oxides may be prepared by heating the hydroxide.*

This method is of general application. (See, however, remarks about silver oxide in (i).) In the case of copper hydroxide, black cupric oxide is formed on warming the hydroxide.

Hydroxides.—Metallic hydroxides may be prepared—(i) *By*

dissolving the oxide in water. This is, of course, only applicable in the case of the soluble oxides, such as sodium, potassium, and calcium oxides.

(ii) *By precipitating the hydroxide from a solution of a salt of the metal by the addition of sodium or potassium hydroxide.* For example—

$$\left.\begin{array}{c}\text{zinc}\\\text{sulphate}\\\text{(soluble)}\end{array}\right\} + \begin{array}{c}\text{sodium}\\\text{hydroxide}\end{array}\right\}\text{form}\left\{\begin{array}{c}\text{zinc}\\\text{hydroxide}\\\text{(insoluble)}\end{array}\right. + \begin{array}{c}\text{sodium}\\\text{sulphate.}\\\text{(soluble)}\end{array}$$
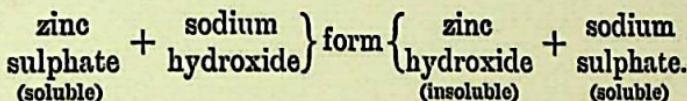
The insoluble hydroxide is then removed from the liquid by filtration.

Salts.—The typical methods for the preparation of salts are—

(i) Dissolve the oxide, hydroxide, or carbonate of the metal, or the metal itself, in the required acid.

(ii) Form the salt required by double decomposition (for insoluble salts only).[1]

(*a*) *Chlorides.*—(i) Silver and mercury are not soluble in hydrochloric acid and with lead the action is very slow. The oxides or carbonates of these metals must therefore be dissolved in hydrochloric acid to obtain the chlorides.

(ii) The insoluble chlorides—lead chloride, silver chloride, and mercury chloride—may be precipitated, from a solution of a salt of the metal required, by the addition to it of hydrochloric acid or a soluble chloride, such as common salt.

$$\left.\begin{array}{c}\text{sodium}\\\text{chloride}\\\text{(soluble)}\end{array}\right. + \begin{array}{c}\text{lead}\\\text{nitrate}\\\text{(soluble)}\end{array}\right\}\text{form}\left\{\begin{array}{c}\text{sodium}\\\text{nitrate}\\\text{(soluble)}\end{array}\right. + \begin{array}{c}\text{lead}\\\text{chloride.}\\\text{(insoluble)}\end{array}$$
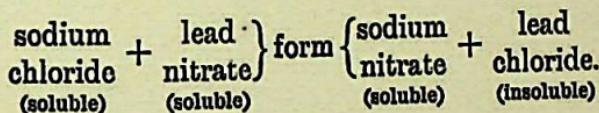
(iii) Zinc chloride, mercurous chloride, cuprous chloride, anhydrous ferric chloride, and other chlorides may be obtained by the action of chlorine upon the required metal (see also pp. 301 and 132).

(*b*) *Sulphates.*—(i) Copper, silver, mercury, and lead are not soluble in sulphuric acid unless the acid is hot and con-

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[1] Or those which can be separated from the solution by fractional crystallization.

centrated. In the preparation of the sulphates of the first three metals, it is advisable to use the carbonate.

(ii) In the preparation of lead sulphate, if sulphuric acid is added to lead carbonate, the outside of the lead carbonate becomes coated with insoluble lead sulphate, which protects the lead carbonate beneath from the action of the sulphuric acid. Hence, in the case of lead, the method of double decomposition is preferable. On the addition of sulphuric acid, or a soluble sulphate to a solution of lead salt, lead sulphate is precipitated, e.g.:

$$\left.\begin{array}{c}\text{lead}\\\text{nitrate}\\\text{\tiny(soluble)}\end{array} + \begin{array}{c}\text{sodium}\\\text{sulphate}\\\text{\tiny(soluble)}\end{array}\right\} \text{form} \left\{\begin{array}{c}\text{lead}\\\text{sulphate}\\\text{\tiny(insoluble)}\end{array} + \begin{array}{c}\text{sodium}\\\text{nitrate.}\\\text{\tiny(soluble)}\end{array}\right.$$
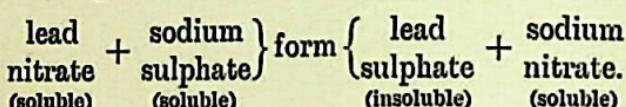
(c) *Nitrates.*—(i) All the metals studied are soluble in nitric acid with the formation of the nitrate, therefore method (i) (p. 305) is of general application.

(ii) All nitrates are soluble in water, therefore method (ii) (p. 305) is unsuitable. The difficulty would be to remove the nitrate required from the solution after it had been formed.

(d) *Carbonates.*—(i) The hydroxide must be dissolved in carbonic acid. The carbonic acid is made and used at the same time by passing a stream of carbon dioxide through a solution of the hydroxide. Even so, the method is only suitable in the case of metals with soluble oxides, namely, sodium, potassium, and calcium (see pp. 91 and 92).

(ii) Since the carbonates, other than sodium and potassium carbonates, are insoluble in water, the method of double decomposition may be employed in their preparation.[1] A solution of sodium carbonate or carbon dioxide is added to a solution of a salt of the required metal. For example—

$$\left.\begin{array}{c}\text{silver}\\\text{nitrate}\end{array} + \begin{array}{c}\text{sodium}\\\text{carbonate}\end{array}\right\} \text{form} \left\{\begin{array}{c}\text{silver}\\\text{carbonate}\\\text{\tiny(insoluble)}\end{array} + \begin{array}{c}\text{sodium}\\\text{nitrate.}\end{array}\right.$$
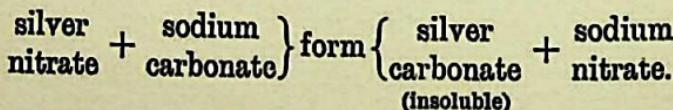
[1] Not applicable in the case of iron, which forms iron hydroxide with sodium carbonate.

Similarly, when carbon dioxide is passed into a solution of lead acetate, the following reaction occurs:—

$$\underbrace{\text{carbon dioxide} + \text{water}}_{\text{carbonic acid}} + \text{lead acetate} \Big\} \text{form} \Big\{ \text{lead carbonate} + \text{acetic acid.}$$
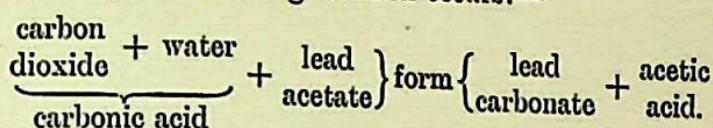
Carbonic acid is such a weak acid, however, that many of the carbonates precipitated by means of sodium carbonate are basic carbonates. For example, copper and lead form basic carbonates when so precipitated.

(c) *Sulphides.*—(i) Owing to the weak nature of the acid hydrogen sulphide (sulphuretted hydrogen), method (i) (p. 305) is unsuitable except in the case of sodium and potassium, which form soluble hydroxides.

On passing sulphuretted hydrogen into sodium hydroxide, the following reaction takes place:—

$$\text{sodium hydroxide} + \text{hydrogen sulphide} \Big\} \text{form} \Big\{ \text{sodium sulphide} + \text{water.}$$
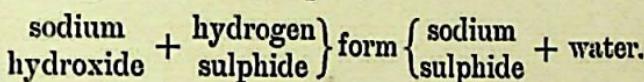
(ii) The insoluble sulphides of copper, silver, mercury ("ic"), and lead may be precipitated by the addition of sulphuretted hydrogen to a solution of a salt of the required metal. For example—

$$\text{copper sulphate} + \text{hydrogen sulphide} \Big\} \text{form} \Big\{ \underset{\text{(insoluble)}}{\text{copper sulphide}} + \text{sulphuric acid.}$$
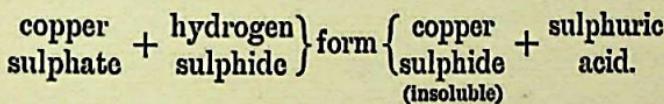
The sulphides of iron and zinc, although insoluble in water, are soluble in dilute acids. Hence, since an acid is set free by the action of sulphuretted hydrogen on a salt (see above), the sulpides of iron and zinc are usually precipitated by the addition of ammonium sulphide to a solution of a salt of the required metal. For example—

$$\text{zinc sulphate} + \text{ammonium sulphide} \Big\} \text{form} \Big\{ \underset{\text{(insoluble)}}{\text{zinc sulphide}} + \text{ammonium sulphate.}$$
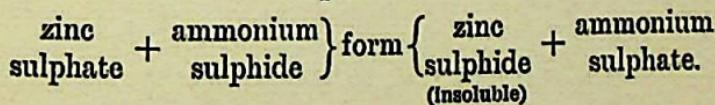
With iron only the ferrous sulphide can be formed in this

way. Ammonium sulphide reduces ferric salts to ferrous salts and then precipitates ferrous sulphide.

CHAPTER XXX

THE PERIODIC CLASSIFICATION OF THE ELEMENTS

Atomic Weights.—In order to account for the Law of Constant Proportions (see p. 79) and the other quantitative "laws" of chemistry, chemists for many years past have *assumed* that all substances are composed of very small particles called atoms. The atoms of any one element are conceived as being alike amongst themselves, but different from the atoms of all other elements. When chemical combination takes place it is viewed as the union of an *integral number* of atoms of each of the elements taking part in the reaction.

For example, when hydrogen and oxygen unite to form water we believe that in the least conceivable particle of water (a molecule) the number of hydrogen atoms is twice as great as the number of oxygen atoms.

It may be that the molecule of water contains (*a*) *two* atoms of hydrogen and *one* atom of oxygen, or (*b*) *four* atoms of hydrogen and *two* atoms of oxygen; but it cannot be that it contains one atom of hydrogen and half an atom of oxygen.

As a matter of fact, we believe that the molecule of water consists of two atoms of hydrogen combined with one atom of oxygen.

Similarly, we believe that the molecule of ammonia consists of three atoms of hydrogen combined with one atom of nitrogen.

Chemists have by very careful experiment obtained the weights of the atoms of the various elements relative to the weight of the atom of hydrogen; that is, the weight of the

atom of hydrogen is taken as unity. The numbers so obtained are called the *atomic weights* of the elements. [In the table on p. 311 the numbers printed below the names of the elements are the approximate atomic weights of those elements.]

On pp. 115 and 119 experiments were described whereby the equivalent of magnesium or zinc could be obtained by the displacement of hydrogen from sulphuric acid by means of the metal.

When an *atom* of zinc displaces hydrogen from sulphuric acid it must displace either one, two, three, or some other integral number of atoms of hydrogen.

If each atom of zinc displaces one atom of hydrogen, then—because (i) the weight of the hydrogen atom is counted as unity, and (ii) the equivalent weight of zinc is the weight of zinc which will displace unit weight of hydrogen: therefore the atomic weight of zinc must be also the equivalent weight of zinc.

But if each atom of zinc displaces two atoms of hydrogen, then for the reasons just given the atomic weight of zinc must be just *double* the equivalent weight. As a matter of fact, the atomic weight of zinc is double the equivalent weight.

The atomic weight of an element is necessarily some simple multiple of the equivalent weight of that element. For example:

Element.	Equivalent weight.	Atomic weight.	Simple multiple.
Hydrogen	1	1	1
Oxygen	7·94	15·88	2
Zinc	32·42	64·85	2
Iron (ferric)	18·5	55·4	3

The reason for mentioning the atomic weights in this chapter is that upon them depends a very important method of classifying the elements, which is due to the work of the chemists Mendeléeff, Newlands, and Meyer.

From what has been stated in Chapter XVIII it will be clear that there is a close relationship between the elements chlorine, bromine, and iodine, both in their physical and chemical properties. These elements (along with fluorine) are for this reason called a "family" of elements, namely, the halogens (see p. 214). A similar but not such a close relationship can also be traced between the members of other "families" of elements. For example, between—

(i) Oxygen and sulphur, &c.
(ii) Nitrogen, phosphorus, arsenic, antimony, and bismuth.
(iii) Carbon and silicon, &c.
(iv) Sodium and potassium, &c.
(v) Copper, silver, and gold (see p. 314).

Mendeléeff in 1869 arranged the elements then known in the order of their atomic weights with a view to finding a more suitable method of classification of the elements than those already in existence. When the elements were arranged in this order he observed that members of each family of elements occurred at fairly regular intervals in the list.

Mendeléeff therefore divided the list of elements, arranged in the order of their atomic weights, into series such that the first members of each series were elements which belonged to the same family (see table on p. 311). He then noticed that the second members of the series formed a second family of allied elements, that the third members belonged to a third family, and so on.

Naturally, gaps had to be left in the table so drawn up, since all the elements had not then been discovered. Some of these gaps have since been filled up, but many yet remain.

In dividing the series into sections it was generally every ninth element which began a new section. Having grouped the elements into these eight groups, it was found advisable to divide the members of each group into two sub-groups, since there was often a greater resemblance between the members of each sub-group than between the sub-groups themselves. For example, in group I, p. 311, the relationship

TABLE OF THE ELEMENTS ARRANGED ACCORDING TO THE PERIODIC CLASSIFICATION

Group I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Hydrogen 1							
			Carbon 12	Nitrogen 14	Oxygen 16		
Sodium 23	Magnesium 24	Aluminium 27	Silicon 28	Phosphorus 31	Sulphur 32	Chlorine 35	
Potassium 39	Calcium 40				Chromium 52	Manganese 55	Iron 56 / Cobalt 59 / Nickel 59
Copper 63	Zinc 65			Arsenic 75		Bromine 80	
	Strontium 87						
Silver 108			Tin 119	Antimony 120		Iodine 126	
	Barium 137						Platinum 195
Gold 197	Mercury 200		Lead 207	Bismuth 208			
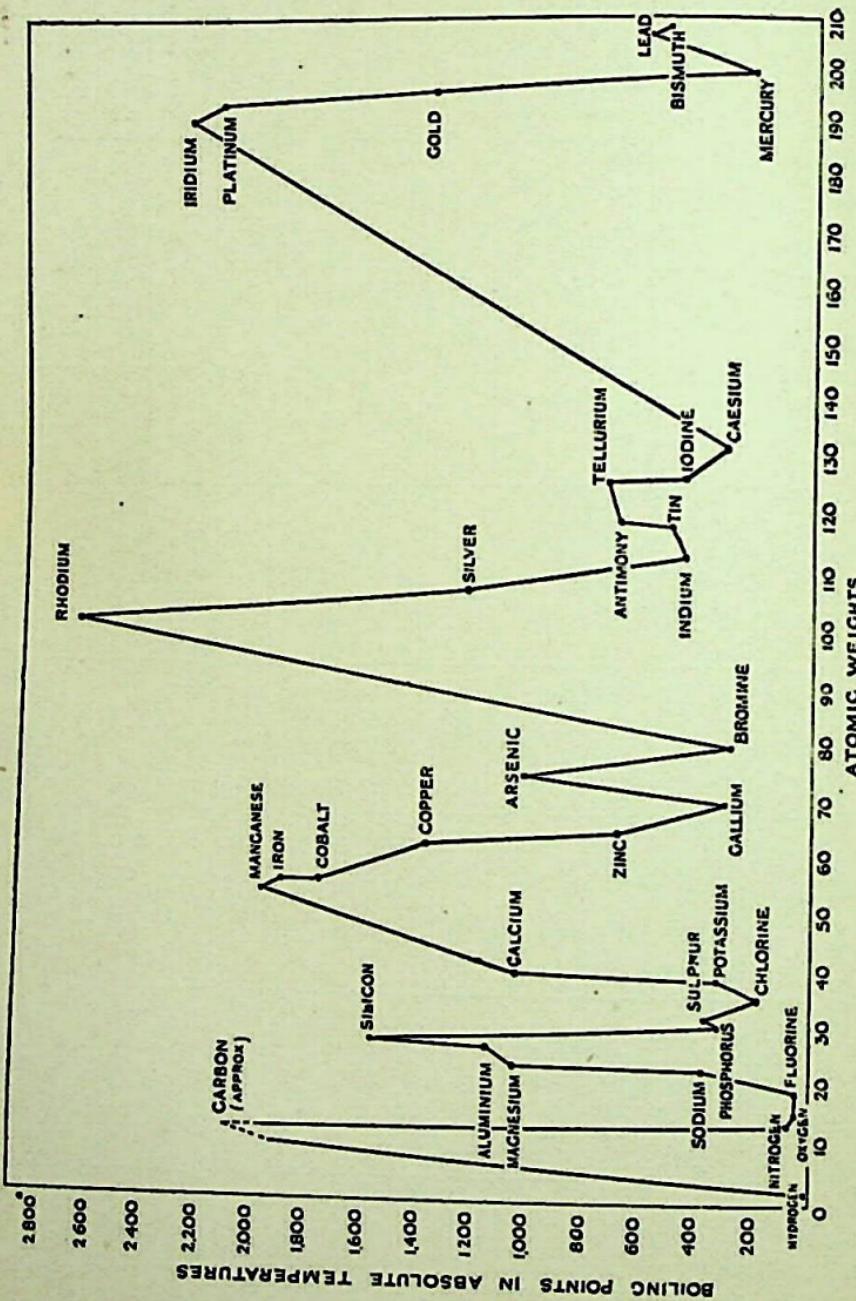
Fig. 119.—Curve of Melting-points of the Elements

between the light metals sodium and potassium, and between the heavy metals copper, silver, and gold, is much closer than that which exists between sodium and copper (see pp. 252 and 280).

The eighth group is irregular. It was found necessary, in order to keep the families of elements in groups, to omit groups of elements when dividing the elements into series or periods of seven elements each. These omitted elements, which themselves form families, were then placed together in the eighth group.

There are several advantages of this periodic classification of the elements.

(i) It serves to bring into prominence the similarity between the chemical and physical properties of the families of elements.

(ii) It also shows the gradual transition of properties of the elements. For example, as we pass along a series from left to right the basic character of the elements becomes less. Thus sodium, magnesium, and aluminium are metals whose basic properties are in descending order. They are followed by the non-metals silicon, phosphorus, sulphur, and chlorine, elements whose acidic properties are in ascending order. The periodic character of the properties of the elements when they are arranged according to their atomic weights may be best seen by plotting the atomic weights of the elements against some property of the elements which can be expressed numerically.

In fig. 119 the atomic weights have been plotted against the boiling-points of the elements.

In fig. 120 the atomic weights have been plotted against the densities of the elements.

In the table given below an attempt has been made to show the relationship between the members of a few of the "families" of elements, and to indicate the corresponding positions which these elements occupy on the curves given in figs. 119 and 120.

ELEMENTS IN THE "FAMILY".	SOME REASONS FOR CALLING THEM A FAMILY.	POSITION OF ELEMENT ON—	
		"MELTING-POINT" CURVE.	"DENSITY" CURVE.
Fluorine, chlorine, bromine, and iodine.	See p. 214	At the minima of the curve.	At (or near) the minima of the curve.
Copper, silver, and gold.	(i) Elements are very malleable and ductile. (ii) Elements are excellent conductors of heat and of electricity. (iii) Elements have small affinity for oxygen, for— (a) They do not readily oxidize in air. (b) They do not decompose water even at high temperatures. (c) They form weak bases. (iv) Elements combine with nitrogen to form unstable nitrides.	On the descending portions of the curve.	On the descending portions of the curve. The density increases with the atomic weight.
Sodium and potassium.	(i) Elements are soft and malleable. (ii) Elements have great affinity for oxygen, for— (a) They readily oxidize in air. (b) They decompose water at ordinary temperatures. (c) They form strong bases. (iii) Elements combine with hydrogen on heating, forming hydrides.	On the ascending portions of the curve. The melting-point decreases as the atomic weight increases.	On the ascending portions of the curve. The density decreases as the atomic weight increases.

Most of the properties of the elements which can be measured, when plotted against the atomic weights of the elements, give curves similar to those in figs. 119 and 120. It has therefore been stated that the properties of the elements are periodic functions of their atomic weights, which means that as the atomic weight increases each property of the elements increases to a maximum, then decreases to a minimum, increases again to a maximum, decreases again, and so on, repeating itself periodically.

This statement is spoken of as the *periodic law*, and the arrangement of the elements just described is called the *periodic classification of the elements*.

APPENDIX

I. EXPERIMENTAL EXAMINATION OF A GAS

(i) What is the colour of the gas?

(ii) Has the gas a distinctive smell?

(iii) Will the gas burn?

(iv) Will the gas support combustion?

(v) Is the gas insoluble, slightly soluble, or very soluble in water?

(vi) Does the gas give an acid or an alkaline or a neutral solution in water?

(vii) What other properties has the gas? (see p. 47).

II. SOLUBILITY OF GASES

100 cu. cm. of water at 0° C. will dissolve approximately—

Nitrogen	2 cu. cm.
Hydrogen	2 ,,
Carbon monoxide	3 ,,
Oxygen	4 ,,
Nitric oxide	7 ,,
Nitrous oxide	130 ,,
Carbon dioxide	180 ,,
Chlorine	300 ,,
Sulphuretted hydrogen	440 ,,
Sulphur dioxide	8,000 ,,
Hydrochloric acid gas	50,300 ,,
Ammonia	114,800 ,,

III. SIMPLE EXERCISES IN MANIPULATION

To Cut off a Piece of Glass Tubing.—Draw the edge of a triangular file across the glass tube *quickly* at the place where it is to be cut. Hold the tube as in the diagram (fig. 121).
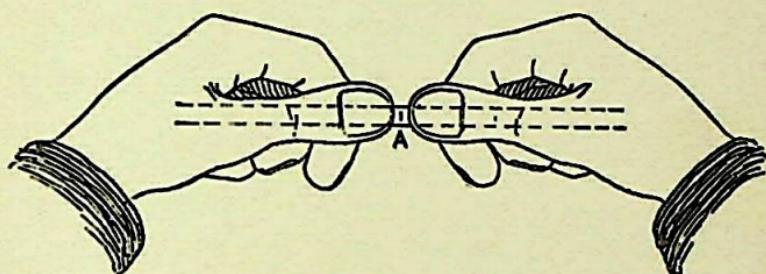
Fig. 121.—A Scratch made by File

Pull the glass tube apart, and at the same time exert a little pressure away from the scratch made by the file. The tube should then break clean across. The cut edges should be
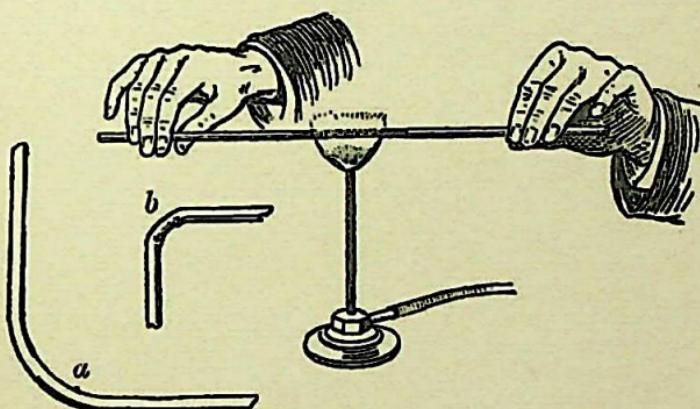
Fig. 122. —Heating a piece of Soft Quill Tube preliminary to Bending

(a) Good bend in flat flame.   (b) Bad bend in Bunsen flame.

rounded by holding them in the Bunsen flame and rotating the tube until the ends begin to melt.

To Bend Narrow Glass Tubing.—Hold the tubing in a bat's-wing flame. Support the tubing as shown in the diagram (fig. 122), and slowly rotate it by rolling it between the thumb

and fingers. When the glass is soft enough to bend under its own weight remove it from the flame and allow it to bend. Do not force the tube, but merely guide it into the required
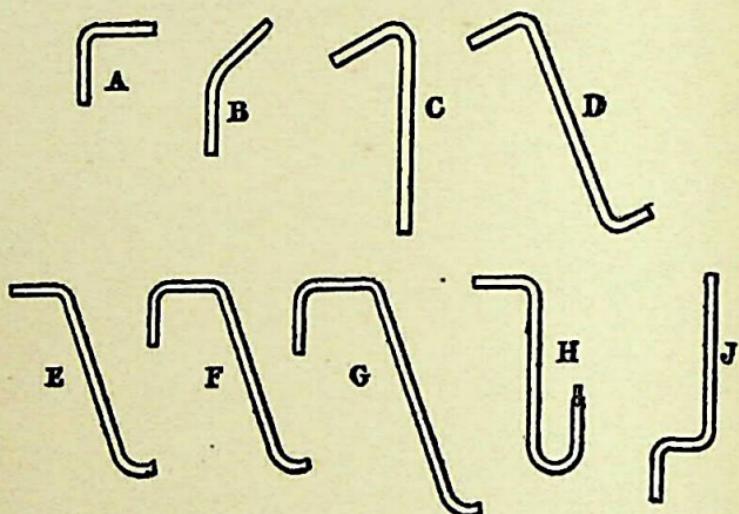
Fig. 123.—Suitable Shapes for Delivery Tubes, &c.

shape. Several shapes which are constantly required in the fitting up of apparatus are shown in fig. 123.

To Close a Piece of Glass Tubing at one End and to make a Bulb Tube.—Hold the tube, as in fig. 122, in the Bunsen
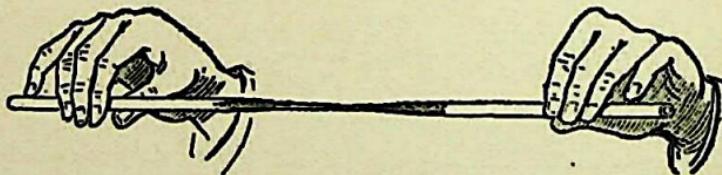
Fig. 124.—Making a Bulb Tube (⅓)

flame just above the tip of the inner cone. Rotate the tube until it softens in the middle. Then withdraw it from the flame and gently pull out each end of the tube (fig. 124).

Break the narrow tube (capillary-tube) at A (fig. 125). Heat the portion C in the Bunsen burner at the point B, and pull off the capillary-tube A B as soon as the glass at B is soft.

Now heat the closed end D in the Bunsen flame, rotating it meanwhile, and when it is quite soft withdraw it from the
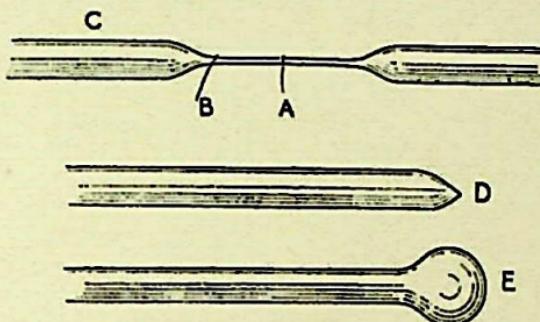
Fig. 125.—Making a Bulb Tube (ii)

flame and blow steadily down the open end until the softened end is expanded into a small bulb (E, fig. 125).

To Bore a Cork.—Select a cork a little too large for the vessel for which it is intended. Roll it on the floor under the
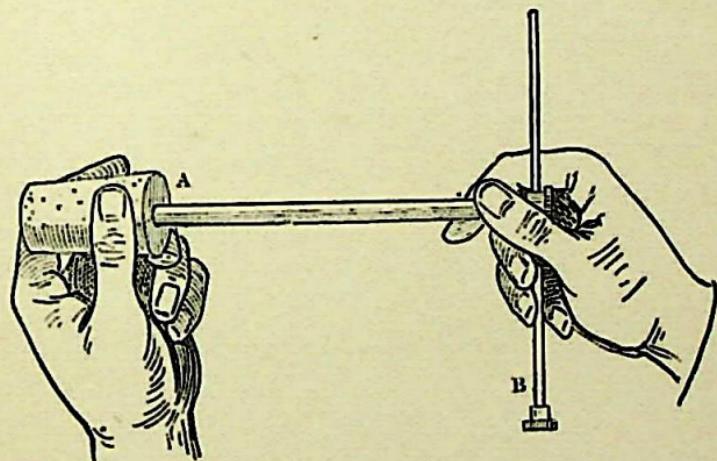
Fig. 126.—Boring a Cork (the student in this illustration has started boring from the *wrong end* of the cork).

sole of your boot to soften it. It should now just fit the vessel tightly. If it does not, roll it again.

Take a cork-borer (fig. 126) and wet the cutting edge A with a little water. Begin at the narrow end of the cork, and bore

a hole nearly through the cork by twisting the cork-borer round and round by means of the handle B. Then complete the hole by boring from the wide end of the cork. This will prevent the cork-borer from dragging a piece out of the cork as it emerges at the wide end.

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